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# ***JPRS Report***

## **Science & Technology**

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***USSR: Chemistry***

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# Science & Technology

## USSR: Chemistry

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**Prize Awarded for Method of Studying Electron Structure and Chemical Bonds of Various Compounds**

18410146c SOVETSKAYA ROSSIYA in Russian  
18 Jan 89 p 3

[Article by Academician S. Vonsovskiy, Sverdlovsk, under the rubric "A Scientist's Opinion: 'Prizes for the Worthy'"]

[Text] The list of works that were accepted for competition for the RSFSR State Prize in science and technology was published in SOVETSKAYA ROSSIYA on 27 December 1988. I wish to voice my thoughts about one of them.

Seventy-five years have passed since x-rays were first broken down into a spectrum. It turned out that the number of lines in the x-ray spectra of each chemical element is relatively small, and their interpretation is much simpler than with optical spectra. This circumstance was instrumental in the intensive development of x-ray spectroscopy and its use in verifying the basic tenets of atomic physics and the zone theory of solids. Of particular interest to chemistry was the discovery of the high sensitivity of x-ray spectra to changes in the nature of chemical bonds of different compounds. However, it was necessary to solve many problems on the road toward practical use of the method for such purposes, and they were related both to the development of methodology and experimental techniques and to comprehension of the nature of the spectra themselves. Soviet scientists—specialists from academy institutions and higher educational institutions of Moscow, Novosibirsk, Sverdlovsk, Leningrad, Kiev and Rostov-on-Don—made a decisive contribution to the solution of these problems; through their joint efforts, which began in the 1960's, ultrasoft and supersoft x-ray spectroscopy, spectroscopy of the quantum yield of the photoeffect, was developed. For the first time anywhere in the world, high-contrast, high-resolution spectra of molecules were obtained and unique equipment was developed....

The authors of this series of studies conducted top-priority investigations of x-ray spectra of many classes of chemical compounds, and the investigations are summarized in 12 monographs. On the basis of the authors' developments, series production of equipment for fine x-ray spectrometry was developed for the first time in the world, and some of it is being delivered abroad. In essence, there has been comprehensive development of a method without which it would be inconceivable today to study the electron structure and chemical bonds of various compounds. There is no doubt that the work in question, "Development of

Theory, Methods and Instruments for X-Ray Spectral Studies of Chemical Bonds," deserves the RSFSR State Prize in science and technology.

UDC 665.61:543

**Trace Elements in Crude Oils of Eastern Georgia**

18410080 Tbilisi SOOBSHCHENIYA AKADEMII NAUK GRUZINSKOY SSSR in Russian  
Vol 131 No 2, Feb 88 (manuscript received 26 Jun 87) pp 313-316

[Article by K. G. Koderdzishvili, M. T. Tkemaladze, T. I. Gabuniya, and N. I. Glonti, Georgian SSR Academy of Sciences, Institute of Physical and Organic Chemistry imeni P. G. Melikishvili]

[Abstract] The quantitative distribution of trace elements in the crude oils of the Samgori, Ninotsninda, and Rustavi deposits and in the Kavtis-Khevi and Kila-Kupra manifestations was studied and compared with data previously obtained for the Norio, Satskhenisi, Taribani, and Ildokani deposits. Preliminary photochemical isolation of trace elements with subsequent ashing was used for all samples except the Kila-Kupra sample, which was ashed directly. All the light oil samples had an ash content of 0.022 percent or less, with the heavy oil samples from Norio and Kila-Kupra having ash contents of 0.0299 and 0.575 percent, respectively. Spectral analysis on a quartz spectrograph was used to determine the V, Ni, Co, Cr, Mn, Cu, Ti, Pb, Sn, Zn, Ba, and Ga levels, which are presented in tabular form. In the Norio, Taribani, Kavtis-Khevi, and particularly Kila-Kupra samples, elevated ash content was accompanied by elevated levels of all trace elements. Trace element levels for the majority of elements were greater than those in their percent abundances in the lithosphere. The V:Ni ratios found ranged from 0.03 to 0.5. Oils from Cretaceous deposits were characterized by elevated Pb and Sn contents, whereas for other elements, there was little difference between Tertiary and Cretaceous oils.

UDC 539.27:541.124.7:541.49

**Electron Structure of 3d-Metal Dihydride Anions**

18410108b Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian  
No 1, Jan 89 (manuscript received 15 Oct 87) pp 81-87

[Article by G. L. Gutsev, Institute of Chemical Physics, USSR Academy of Sciences, Chernogolovka]

[Abstract] The purpose of this work was to calculate the electron and geometric structure of 3d-metal dihydride anions by a discrete-variational  $X_\alpha$  method and to determine the behavioral peculiarities of the anions' electron characteristics as they move along the series. The results of computation of the first anion ionization potentials

are in good agreement with the previously known experimental quantities. The electron affinity of  $\text{MH}_2$  molecules, which is close to the primary ionization potentials of the corresponding anions, changes nonmonotonically with movement along the 3d-metal series due to the smallness of the adiabatic corrections. The electron affinity of 3d-metal dihydrides is always greater than the electron affinity of the central atom is, but changes in these quantities in that the series are symbiotic. Figures 2, references 16: Western.

UDC 541.124.7:539.27:541.49:546.641:546.831

**Electron Structure and Optical Absorption Spectra of  $\text{Y}_2$  and  $\text{Zr}_2$  Dimers**  
18410108c Moscow IZVESTIYA AKADEMII NAUK  
SSSR: SERIYA KHMICHESKAYA in Russian  
No 1, Jan 89 (manuscript received 26 Oct 87) pp 87-91

[Article by G. L. Gutsev, Institute of Chemical Physics, USSR Academy of Sciences, Chernogolovka]

[Abstract] The purpose of this work was to calculate the electron structure, ionization potential with valent levels, and energies of optical transitions within the framework of a single approach—the discrete-variational  $X_\alpha$  method. According to the data calculated within the framework of the discrete-variational  $X_\alpha$  method, the basic state of the dimers  $\text{Y}_2$  and  $\text{Zr}_2$  is the symmetry  ${}^1\Sigma_g^+$  state, while the atoms in the dimers have a high-spin  $4d^{n+1} 5s^1$  configuration. The chemical bond in  $\text{Y}_2$  has a primarily  $5s$ - $5s$  nature, manifested as great interatomic separation; involvement in the bond of 4d electrons leads to a significant reduction in bond length in the  $\text{Zr}_2$  dimer. The theoretical optical absorption spectrum of the  $\text{Zr}_2$  molecule agrees well with the experimentally determined spectrum of this molecule isolated in an argon matrix. Figures 2, references 14: 4 Russian, 10 Western.

UDC 541.127:541.183

**Sorption of Metal Ions From Seawater on Clinoptilolyte From Various Deposits**  
18410112a Moscow IZVESTIYA AKADEMII NAUK  
SSSR: SERIYA KHMICHESKAYA in Russian  
No 11, Nov 88 (manuscript received  
22 Jun 87) pp 2461-2466

[Article by R. Kh. Khamizov, T. Yu. Butenko, L. V. Bronov, V. V. Skovsky, and V. A. Novikova, Institute of Geochemistry and Analytic Chemistry imeni V. I. Vernadskiy, USSR Academy of Sciences, Moscow; Institute of Chemistry, Far-Eastern Science Center, USSR Academy of Sciences, Vladivostok; Southern Sakhalin State Pedagogic Institute]

[Abstract] A study is made of the sorption of metal ions from seawater onto various clinoptilolyte specimens in order to select the most promising sorbents for extraction of strontium and rubidium. The sorption kinetics

were studied in a column with a cross-sectional area of  $130 \text{ cm}^2$  and a height of 30 cm. Seawater was passed through the column for 400-600 hours in a fluidized bed mode at about  $1,000 \text{ h}^{-1}$ . Metal ions were determined in the regeneration solutions by atomic absorption analysis. The rate-limiting stage in the kinetics of the sorption of metal ions from seawater is found to be internal diffusion. The distribution coefficients and one-time separation coefficients of the metal ions and sorption selectivity sequence are determined. All the clinoptilolites studied can be used for the primary concentration of rubidium from seawater. Zeolites from the Dzegvi and Tedzami deposits should be used for the concentration of strontium. The differences in selectivity are apparently related to the composition of macrocations and the content of nonexchange  $\text{K}^+$  and  $\text{Mg}^{2+}$  ions. Figures 2, references 13: 10 Russian, 3 Western.

UDC 547.565:542.951.8

**Some Properties of Nitrosoresorcines**  
18410153b Tallinn IZVESTIYA AKADEMII NAUK  
ESTONSKOY SSR: KHIMIYA in Russian  
Vol 38 No 1, Jan-Mar 89 (manuscript received  
5 Jul 88) pp 17-20

[Article by I. Johannes and L. Molder, Institute of Chemistry, EstSSR Academy of Sciences]

[Abstract] Five mono- and dinitroso derivatives of resorcinol were synthesized from resorcinols obtained from the breakdown of shale oil: 4-nitroso-2,5-dimethylresorcinol; 2,4-dinitrosoresorcinol and 2,4-dinitroso-5-methylresorcinol. Their optical properties, acid dissociation constants, the solubility expressed as a function of pH and its temperature dependence were determined and tabulated. Figure: 1; references 5: 4 Russian, 1 Western.

UDC 539.54

**Analysis of Nonstationary Substance Flow: Potential Uses of Computerized Chromatography**  
18410153c Tallinn IZVESTIYA AKADEMII NAUK  
ESTONSKOY SSR: KHIMIYA in Russian  
Vol 38 No 1, Jan-Mar 89 (manuscript received  
19 May 88) pp 25-33

[Article by M. Kalyurand, Institute of Chemistry, EstSSR Academy of Sciences]

[Abstract] The relationship between the rate of the change of an investigated process and time resolution of the analytical method used, was discussed. An attempt was made to show how computerized chromatography experiment makes it possible to organize the determinations according to this new approach, decreasing two-three fold the required time for analysis. It was shown that the Kotelnikov's theorem was applicable to the case under investigation: "if a frequency  $f_m$  can be found at which  $F(f)=0$  for any  $f < f_m$ , then  $\Delta t$  should be selected so that the condition  $\Delta t >$  or equal to  $1/(2f_m)$  would be

satisfied." Specifically, it was shown that a chromatographic analysis of a mixture of nonstationary gas flow and liquid is possible to be performed within 0.15 sec if the stroboscopic sampling method is used. The use of PC's to control this process is necessary. Further time decrease could be achieved in the future. This method should find applications in analysis of the vapor phase of various reactive systems, such as thermal destruction or catalytic processes occurring on the surface of solids, or thermodesorption under conditions of rapid programmed heating. Figures 4; references 23: 7 Russian (1 Russian (1 by Western author), 16 Western (2 by Russian authors).

UDC 632.95.021;632.981.13

**Use of Juvenoids with Microdoses of Insecticides to Enhance Effectiveness of Greenhouse White Fly Control**

*18410153d Tallinn IZVESTIYA AKADEMII NAUK ESTONSKOY SSR: KHIMIYA in Russian Vol 38 No 1, Jan-Mar 89 (manuscript received 2 Apr 88) pp 40-43*

[Article by S. Novikova, V. Burov, K. Leyets, I. Kudryavtsev, and T. Liiv, All Union Scientific Research Institute of Plant Protection, Institute of Chemistry, EstSSR Academy of Sciences]

[Abstract] Effect of juvenoid preparation ephoxen used in combination with microdoses of two organophosphoric insecticides: diazinone and actelic, was evaluated as a control measure against greenhouse white fly. A synergistic effect was achieved with such a combination: the larvae died due to the toxic effect of the preparation, the

puparia and imagos died because of the induced hormonal imbalance. Because of the synergism, the juvenoid dose could be reduced 2-fold and that of the insecticides 10-fold while retaining the same results as with the individual reagents. Further studies are needed to refine the dosage and possibly to extend the assortment of insecticides to achieve the desired results with minimal phytotoxicity. Figure 1; references 6: 3 Russian, 3 Western.

UDC 677.3+543.42

**Investigation of Flame Resistant Wool Fibers by an IR-Spectroscopic Method**

*18410153e Tallinn IZVESTIYA AKADEMII NAUK ESTONSKOY SSR: KHIMIYA in Russian Vol 38 No 1, Jan-Mar 89 (manuscript received 23 Jun 88) pp 47-50*

[Article by O. Lirret and L. Lakhe, Institute of Chemistry, EstSSR Academy of Sciences]

[Abstract] IR spectroscopy was applied in an analysis of wool modified with various additives, using the 9  $\mu\text{m}$  spectrum range in which the amide bands were not superimposable. Analyses were performed on natural wool and wool treated with 10 percent solution of  $\text{K}_2\text{TiF}_6$ , 39.4 percent chloroendicoic acid [this is actually a transliteration, I could not find this term in my dictionaries: IJM] and a combination of 10 percent of both of these reagents. Characteristics bands appearing and disappearing upon pyrolysis of the experimental samples were noted. It was concluded that the IR spectroscopic method can be used effectively in analysis of flame resistant wool fibers to evaluate action of antipyrenes and even to identify their mechanism of action. Figures 5; references 7: 1 Russian, 6 Western.

UDC 66.097.3.012.46

**Improving Technology of Hydrocarbon Conversion Catalyst Carrier**

18410085b Kiev KHIMICHESKAYA

TEKHOLOGIYA:

NAUCHNO-PROIZVODSTVENNYY SBORNIK in Russian No 6, Nov-Dec 88 (manuscript received 28 Sep 87) pp 17-20

[Article by T. A. Levanyuk, G. A. Chernaya, V. V. Veselov, and A. F. Babikov, Institute of Gas, Ukrainian Academy of Sciences, Kiev]

[Abstract] The following compounds were studied as additives to milled alumina for use in the catalytic conversion of hydrocarbon materials as carriers: calcium oxide, up to 5 percent; SD-2 alkaline binder, up to 4 percent; and sodium carboxymethyl cellulose, up to 2 percent. The molding mass was mixed in water, extruded into cylindrical granules, dried for 16 hours at 20-25°C and 8 hours at 100°C, and heated for 4 hours at 1,360°C. The strength and porosity of the granules were then determined. The introduction of over 3 percent CaO was found to decrease the strength of the granules. Their strength was increased by 2-4 percent carboxymethyl cellulose after drying; however, it decreased after further heating. SD-2 increases the strength of granules significantly, the maximum being reached at 2 percent of the additive. This same SD-2 content also corresponds to the minimum porosity. All specimens had a porosity of over 20 percent. Thermal stability is best with 2 percent SD-2 and 3 percent carboxymethyl cellulose. The optimal carrier contains (percent): alumina, 91; CaO, 3; MgO, 1; SD-2, 2; carboxymethyl cellulose, 3. Figures 3, references 3: Russian.

UDC 66.094.14:[661.7:547.532]

**Hydrogenation of Benzene in Continuous-Flow Mode on Ruthenium Catalyst**

18410087a Moscow KHIMICHESKAYA

PROMYSHLENNOST in Russian

No 11, Nov 88 pp 671-672

[Article by Ye. Yelemesov, B. T. Utelbayev, A. M. Kolchin, P. P. Zanozina, and B. Zh. Zhanabayev]

[Abstract] Liquid-phase hydrogenation of benzene was studied in a stationary layer of 0.5-1 percent Ru catalyst on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, which was intended to produce chromatographically pure cyclohexane.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> carrier granules 10-11 mm long and 3 mm in diameter were saturated with an aqueous solution of Ru(OH)Cl<sub>3</sub>, the water was evaporated, and the catalyst was reduced with 40 percent aqueous formaline and then dried in air at 130-140°C for 2 hours. It was then activated in a current of hydrogen. Hydrogenation was performed in a column-type electrically heated laboratory installation developed by the authors. It was 2 cm in diameter, and the catalytic chamber had a height of 45 cm. The catalyst retained its activity for 400 hours at 90-120°C

at a hydrogen pressure of 0.5 MPa, a benzene feed rate of 0.2 hr<sup>-1</sup>, and a molar hydrogen:benzene ratio of 3-5:1 (producing 100 percent cyclohexane). Figures 2, references 7: 5 Russian, 2 Western.

UDC 66.094.17:[661.7:547.724.1]

**Hydrogenation of Furfural on Multicomponent Copper Catalysts**

18410087b Moscow KHIMICHESKAYA

PROMYSHLENNOST in Russian

No 11, Nov 88 pp 672-673

[Article by L. D. Plyusnin, T. Beysekov, M. S. Yerzhanova, and B. D. Daurenbekov]

[Abstract] The process of the hydrogenation of furfural was studied on skeletal copper catalysts produced from Cu-Al alloy with the addition of ferrochrome and ferrotitanium in a high-frequency melting furnace. The alloy contained 37-46 percent copper, 1-10 percent ferrotitanium, 50 percent aluminum, and 3 percent ferrochrome. Catalysts were produced by soaking in a 20 percent aqueous caustic soda solution in a boiling water bath for 1 hour. Experiments were performed in a 250 cm<sup>3</sup> autoclave with intensive agitation at 40-180°C and from 4 to 12 MPa hydrogen pressure. The catalysts were found to be highly active and selective for liquid-phase furfural hydrogenation, and they were superior in productivity and stability to type GIPKh-105 catalyst. Figures 3; references 8: 7 Russian, 1 Western.

UDC 541.128.13

**Interactions of Carbon and Nitrogen Oxides on Palladium Catalysts**

18410111c Kiev UKRAINSKIY KHIMICHESKIY

ZHURNAL in Russian Vol 54 No 11, Nov 88

(manuscript received 10 Feb 87) pp 1147-1151

[Article by M. G. Martsenyuk-Kukharuk, S. N. Orlik, V. A. Ostapuk, and Yu. I. Pyatnitskiy, Institute of Physical Chemistry, Ukrainian Academy of Sciences, Kiev]

[Abstract] Results are presented from a study of the reactions of CO and NO on a palladium catalyst. Studies were performed in a 0-gradient reactor at atmospheric pressure with helium as the diluting gas. The concentrations of the reaction mixture components were not over 1.5 percent by volume except in one series of experiments in which the initial CO concentration was 8 percent. Selectivity of the process for N<sub>2</sub> increases with increasing temperature. In the presence of hydrogen, conversion of CO to CO<sub>2</sub> and NO to nitrogen-containing products is faster. Water vapor has practically no influence on the rate of the reaction between CO and NO, whereas the addition of SO<sub>2</sub> significantly inhibits the process. A mechanism for the process is suggested. The fact that water vapor does not influence the process

indicates that it is not significantly adsorbed on the catalyst under the conditions tested, in contrast to  $\text{SO}_2$ , which inhibits the process. Figures 3, references 12: 9 Russian, 3 Western.

UDC 541.128.13:539.192

**IR Spectroscopic and Quantum Chemical Study of Reaction of Acetone and Acetonitrile Molecules With Metal Catalyst Surface**

18410106a Kiev TEORETICHESKAYA I  
EKSPERIMENTALNAYA KHIMIYA in Russian  
Vol 24 No 5, Sep-Oct 88 (manuscript received  
7 May 87) pp 545-552

[Article by G. I. Golodets, N. V. Pavlenko, V. M. Gunko, and G. M. Telbiz, Institute of Physical Chemistry imeni L. V. Pisarzhevskiy, Ukrainian Academy of Sciences, Kiev]

[Abstract] An IR spectroscopic and quantum chemical study is performed of the adsorption of acetone and acetonitrile on the surfaces of some transition metals in order to determine the most probable structure of the M-R complex and its energy characteristics. It is found that the primary form of the bond between acetone and acetonitrile and the transition metals is dative interaction in which the d-electrons of the metal are located in the p'-orbitals of the molecules' functional groups. Formation of a donor-acceptor complex is also possible by the transfer of  $\pi$ -electrons from the ketone molecule to the free d-orbitals of the metal. The activation of the molecules and the nature of the intermediate  $Z_{\text{R}}\text{RH}$  complex apparently differ for the two compounds under the experimental conditions in spite of the obvious analogy of the electron structure of the molecules. Figures 4, references 21: 17 Russian, 4 Western.

UDC 541.128.13

**Strong Metal-Carrier Interaction Rules as Exemplified by Influence of Vanadium Oxide on Catalytic Activity of Platinum Metals in Hydrogenation of CO**

18410106b Kiev TEORETICHESKAYA I  
EKSPERIMENTALNAYA KHIMIYA in Russian  
Vol 24 No 5 Sep-Oct 88 (manuscript received  
30 Jan 87) pp 612-616

[Article by N. I. Ilchenko, Yu. I. Shmyrko, L. N. Rayevskaya, and G. I. Golodets, Institute of Physical Chemistry imeni L. V. Pisarzhevskiy, Ukrainian Academy of Sciences, Kiev]

[Abstract] An attempt is made to determine the nature and degree of influence of an oxide additive on the catalytic properties of transition metals of various chemical natures and to determine the principal physical and chemical properties of metals that determine the direction of the change in their catalytic activity and selectivity. Vanadium oxide was selected as the additive because

of earlier reports of nonadditive catalytic activity in the system Pt-V<sub>2</sub>O<sub>5</sub> in reactions involving H<sub>2</sub>. The factor determining the change in catalytic properties of platinum metals under the influence of vanadium oxide is found to be the change in the energy of the M-CO bond due to the strong interaction of the metal with V<sub>2</sub>O<sub>5-x</sub>. The value of  $q_{\text{CO}}$  is determined to a great extent by the oxidation of the transition metal and by the ability of the metal to give up electrons to an oxide or take electrons from an oxide. The higher the electron-donor capacity, the weaker the bond of CO with the surface of the metal and the higher the catalytic activity. Figures 4, references 10: 9 Russian, 1 Western.

UDC 521.128.13

**Catalytic and Adsorption Properties of Iron-Nickel Catalysts in Synthesis of Ammonia**

18410106 Kiev TEORETICHESKAYA I  
EKSPERIMENTALNAYA KHIMIYA in Russian  
Vol 24 No 5, Sep-Oct 88 (manuscript received  
16 Feb 87) pp 616-618

[Article by V. K. Yatsimirskiy, Ye. V. Ishchenko, T. B. Mischanuk, and Zo Zen Kho, Kiev University]

[Abstract] The properties of nitrogen chemisorbed on the surface during the course of a catalytic reaction are studied. Iron-nickel catalysts were reduced by carefully purified nitrogen-hydrogen mixtures of stoichiometric composition at atmospheric pressure for 12 hours with temperature gradually increasing from 523 to 723K. The status of the adsorbed nitrogen was then studied by the thermal desorption method. The most active catalyst, pure iron, is found to have two forms of chemisorbed nitrogen, one dissolved in the surface layer and the other adsorbed onto the surface. The adsorbed form is responsible for catalysis. The mechanism of activation of molecular nitrogen during the catalytic synthesis of ammonia, destabilization of the nitrogen-nitrogen bond, is more effective in polyatomic iron clusters. Figures 2, references 8: 7 Russian, 1 Western.

UDC 542.971.3:547.217.6

**Conversion of N-Dodecane With Oxygen on Aluminum-Vanadium Catalyst**

18410108a Moscow IZVESTIYA AKADEMII NAUK  
SSSR: SERIYA KHIMICHESKAYA in Russian  
No 1, Jan 89 (manuscript received 13 Jul 87) pp 16-20

[Article by O. D. Sterligov, N. I. Rybakova, S. V. Adelson, and G. V. Isagulyants, Institute of Organic Chemistry imeni N. D. Zelinskiy, USSR Academy of Sciences, Moscow; Moscow Institute of Oil and Gas imeni I. M. Gubkin]

[Abstract] A study is made of the reaction of the formation of olefins from n-dodecane in the presence of O<sub>2</sub> on an aluminum-vanadium catalyst. Increasing the dilution

of n-dodecane by water vapor showed that the conversion of n-dodecane and olefin selectivity first increased slightly and then decreased. The greatest selectivity was obtained at a molar dilution of 4. This same dilution produced the maximum yield of  $C_{12}$  and total  $C_{6-12}$  olefins. Increasing dilution decreased the conversion of  $O_2$  and inhibited cracking and deep oxidation, reducing the yield of  $C_{6-11}$  and  $C_{1-5}$  hydrocarbons as well as the total yield of CO and  $CO_2$ . The formation of n-dodecenes from n-dodecane on an aluminum-vanadium catalyst occurs by dehydrogenation and oxidative dehydrogenation, while  $C_{6-11}$  olefins are formed by oxidative cracking of hydrocarbons. Under optimal conditions, a 15 percent yield of  $C_{6-12}$  olefins is achieved, including about 10 percent n-dodecenes, with a selectivity of 70 percent. The  $C_{6-11}$  hydrocarbons contained approximately equal quantities of paraffins and olefins, with the  $C_{7-9}$  hydrocarbons being most abundant. Figures 3, references 16: 12 Russian, 4 Western.

UDC 541.128.12'13:542.943.7:547.592.20:  
541.124.2:542.978:546.784'23

#### Kinetic Method of Determining Radical Formation Rate Upon Catalytic Oxidation by Heterogeneous Inhibitor

18410110b Moscow KINETIKA I KATALIZ in Russian  
Vol 29 No 5, Sep-Oct 88 (manuscript received  
19 Jun 87) pp 1098-1104

[Article by A. L. Smirnova, L. A. Tavadyan, and E. A. Blyumberg, Institute of Chemical Physics, USSR Academy of Sciences, Moscow]

[Abstract] A method of measuring the rate of formation of a chain by means of a heterogeneous tungsten selenide inhibitor is suggested and used under homogeneous and heterogeneous catalysis conditions. Model systems include oxidation of cyclohexene in the presence of manganese molybdate and copper selenide. Oxidation was performed at 70°C and 50°C on a manometric installation in a reactor with a magnetic stirrer in a chlorobenzene solution. The reaction mechanism of the oxidation of  $C_6H_{10}$  is suggested, including all reactions that can occur in the presence of  $WSe_2$  and one of the heterogeneous catalysts. The value of  $W_i = 8.6 \cdot 10^{-7}$  mol/l/s agrees satisfactorily with the rate of radical formation in the process determined in a previous work by the same author by another method. Figures 3, references 8: Russian.

UDC 542.973:541.183:542.943.7'952.6

#### Oxide Catalysts for Gas Purification From Easily Polymerized Impurities

18410110c Moscow KINETIKA I KATALIZ in Russian  
Vol 29 No 5, Sep-Oct 88 (manuscript received  
29 Jul 87) pp 1155-1161

[Article by A. A. Yevstratov, V. M. Pomerantsev, and A. F. Tubolkin, Leningrad Institute of Technology imeni Lensovet]

[Abstract] Low-temperature catalytic purification of gases to remove unsaturated organic compounds is studied by using oxide double-action catalysts active in

polymerization and deep oxidation reactions. The activity of the catalysts during gas purification was studied on a flow-through installation with an inside reactor diameter of  $2 \cdot 10^{-2}$  m, a catalyst layer volume of  $5 \cdot 10^{-6}$  m<sup>3</sup>, a temperature of 200°C, and a particle size of  $0.5-1.0 \cdot 10^{-3}$  m. Results of the analysis of the chromium-oxide catalyst are presented in tabular form. It is confirmed that the condensation products are high-molecular mass compounds formed upon concentration of the contaminants. Figures 4, references 21: 16 Russian, 5 Western.

UDC 541.128.3:542.941.8:547.592.12:546.92-  
44:541.183

#### Supported Platinum Carbonyl Catalysts. I. Preparation and Catalytic Activity in Dehydrogenation of Cyclohexane

18410110d Moscow KINETIKA I KATALIZ in Russian  
Vol 29 No 5 Sep-Oct 88 (manuscript received  
26 May 87) pp 1169-1173

[Article by N. M. Ostrovskiy, O. V. Oshchurkova, O. B. Bogomolova, and N. B. Shitova, Omsk Department, Institute of Catalysis, Siberian Division, USSR Academy of Sciences]

[Abstract] A method is described for applying platinum dicarbonyl on carbon and aluminum oxide. The adsorption properties of the dicarbonyl were studied for activated carbon and  $\gamma-Al_2O_3$  following heating to 100°C for 1 hour in a vacuum. The catalytic activity was determined in benzene at 280-320°C with a 5 and 85 percent conversion. The specific activity of Pt catalysts in the dehydrogenation of cyclohexane is determined primarily by the structure of the surface of the supported crystals. Other factors influence the process only to the extent that they form the crystal structures. Figures 1, references 26: 12 Russian, 14 Western.

UDC 46.623'655'55-44:541.183:546.21-128.2.024:  
543.878:539.196:543.422

#### Influence of Electron Metal-Oxide Interaction on Reactivity of Adsorbed Oxygen Radicals. Supported Catalysts Containing Cerium Oxide and Cu, Ag, Au

18410110e Moscow KINETIKA I KATALIZ in Russian  
Vol 29 No 5, Sep-Oct 88 (manuscript received  
10 Sep 87) pp 1181-1188

[Article by A. L. Tarasov, L. K. Przhevalskaya, V. A. Shvets, and V. B. Kazanskiy, Institute of Organic Chemistry imeni N. D. Zelinskiy, USSR Academy of Sciences, Moscow]

[Abstract] The EPR method is used to study the reactivity of anion radicals relative to  $O_2^-$  that are adsorbed on the surface of an aluminum-cerium catalyst with Cu, Ag, and Au additives. The activity is several orders of magnitude greater than for catalysts without these additives. An explanation is suggested for the phenomenon of

increasing reactivity of oxygen radicals adsorbed on semiconductors in the presence of a metal. The explanation makes an allowance for the electron interaction between the metal and the semiconductor. The influence of electron interactions is primarily felt in its effect on the properties of the oxide and particles adsorbed onto its surface and results from the significantly greater concentration of electrons in the metal than in the semiconductor oxide. Transformation of even a very small fraction of the electrons of the metal through the barrier to the acceptor levels of the oxide therefore has a significant influence on their properties. Figures 5, references 12: 10 Russian, 2 Western.

UDC 541.183:538.971:[546.26-162+546.93]-44:543.51

**Graphitization of Carbon on Iridium Surface**  
*18410110f Moscow KINETIKA I KATALIZ in Russian  
Vol 29 No 5, Sep-Oct 88 (manuscript received  
31 Jul 87) pp 1196-1201*

[Article by N. R. Gall, S. N. Mikhaylov, Ye. V. Rutkov, and A. Ya. Tontegode, Institute of Physics and Technology imeni A. F. Ioffe, USSR Academy of Sciences, Leningrad]

[Abstract] A study is made of the graphitization of carbon on the surface of Ir in two ultra-high-vacuum metal installations, an electronic Auger spectrometer, and a magnetic mass spectrometer. It is shown that graphitization in the adsorption layer is most effective at a temperature of less than 1,000K, when the surface carbon is present as chemisorbed atoms. When clusters of carbon are present, graphitization is difficult and occurs only at 1,100-1,500K or higher. Since the migration of carbon atoms occurs effectively at 900K, this presents no obstacle to the formation of densely packed chemisorbed carbon islands at the edge of an atomic step. Figures 3, references 20: 13 Russian, 7 Western.

UDC 541.128:542.941.7:547.364.4

**Hydrogenation of Acetylene-Ethylene Alcohols on Membrane Palladium-Ruthenium Alloy Catalyst**  
*18410112b Moscow IZVESTIYA AKADEMII NAUK  
SSSR: SERIYA KHIMICHESKAYA in Russian  
No 11, Nov 88 (manuscript received  
27 Apr 87) pp 2469-2473*

[Article by A. N. Karavanov and V. M. Gryaznov, Institute of Petrochemical Synthesis imeni A. V. Topchiyev, USSR Academy of Sciences, Moscow]

[Abstract] Results are presented from a study of the processes of the hydrogenation of 3-methylpentene-4-ine-1-ol-3, 3-methylpentene-3-ine-1-ol-5, and 2,6-dimethyloctene-2-ine-7-ol-6 on a membrane catalyst of an alloy of Pd with 6 mass percent Ru. It is found that the kinetics of the hydrogenation of acetylene-ethylene alcohols are similar to those of acetylene alcohols. The rate of hydrogenation of the acetylene bonds of the eninols

depends on their structure. When conjugate eninols are hydrogenated, the primary reaction is 1,2-attachment of hydrogen at the acetylene bond, while hydrogenation of conjugate dienols occurs largely by 1,4-attachment of hydrogen. Deuteration of dehydrolinalol on the membrane catalyst shows no H/D exchange in the substrate at over 50 percent conversion. A mechanism of the hydrogenation of acetylene alcohols on the membrane Pd-alloy catalysts is suggested. Figure 1, references 8: 5 Russian, 3 Western.

UDC 541.128:542.91:547.217.5

### Synthesis of Hydrocarbons From CO and H<sub>2</sub> on Co-Mixed Oxide Catalysts

*18410112c Moscow IZVESTIYA AKADEMII NAUK  
SSSR: SERIYA KHIMICHESKAYA in Russian  
No 11, Nov 88 (manuscript received  
22 Jul 87) pp 2474-2477*

[Article by T. V. Khlebnikova, A. Yu. Krylova, S. D. Sominskiy, and A. L. Lapidus, Institute of Organic Chemistry imeni N. D. Zelinskiy, USSR Academy of Sciences, Moscow]

[Abstract] A study is made of the interaction of the SiO<sub>2</sub> carrier component with MgO, BeO, MnO<sub>2</sub>, and ZrO<sub>2</sub> and its influence on the activity and selectivity of Co-catalysts used in the synthesis of hydrocarbons from CO and H<sub>2</sub>. Carriers were obtained by saturating silica gel-type KSM-6p with nitrates of Be, Mg, Zr, and Mn with subsequent heating to 500°C. Basic cobalt carbonate was then mixed with the carrier at CO-carrier=1:2 and reduced in H<sub>2</sub> at 450°C for 4 hours at V=100 hr<sup>-1</sup>. Experiments were conducted in a counterflow catalytic installation at atmospheric pressure, CO:H<sub>2</sub>=1:2 by volume, V=100 hr<sup>-1</sup>. The use of binary carriers of the oxides of silicon and Mg, Be, Zr, and Mn for Co catalysts increased their activity and selectivity in comparison with individual oxides and increased the content of isoparaffins and C<sub>11</sub>-C<sub>18</sub> hydrocarbons in the catalyst. Figures 2, references 5: Russian.

UDC 541.128.13:546.92:542.941.7:546.262.3-31

**Catalytic Activity of Platinum on Carbon Fiber Materials in Hydrogenation of Carbon Monoxide**  
*18410112d Moscow IZVESTIYA AKADEMII NAUK  
SSSR: SERIYA KHIMICHESKAYA in Russian  
No 11, Nov 88 (manuscript received  
13 Jul 87) pp 2478-2481*

[Article by A. L. Lapidus, O. A. Malykh, A. Yu. Krylova, and G. I. Yemelyanova, Institute of Organic Chemistry imeni N. D. Zelinskiy, USSR Academy of Sciences, Moscow]

[Abstract] A study was made of the activity of platinum catalysts on carbon fibers in the hydrogenation of CO. The catalysts were prepared by saturating the carriers

with aqueous solutions of  $H_2PtCl_6$  or platinum ammoniate, dried 10-12 hours at 100-110°C, and then reduced in a current of  $H_2$  for 5 hours. Hydrogenation of CO was performed in a flow-through installation at atmospheric pressure at a  $CO:H_2$  ratio of 1:2 by volume at 200-600°C with a CO conversion rate of about 5-10 percent. The initial substances and reaction products were analyzed by gas chromatography. It was found that platinum applied to carbon fiber fabric is active in the hydrogenation of carbon monoxide, with the activity depending on the platinum content in the specimen. The quantity of platinum applied to the carbon fiber depends on the acid-basic properties of the carbon fiber surface. Figure 1, references 11: 6 Russian, 5 Western.

UDC 66.095.253.73.001.4:[661.7:547.532]

### Pilot-Scale Testing of Alkylation Catalyst Using Domestic Carriers

18410120b Moscow KHIMICHESKAYA PROMYSHLENNOST in Russian  
No 10, Oct 88 pp 596-597

[Article by Yu. I. Kozorezov, A. L. Mikrtchan, and V. I. Lisin]

[Abstract] Pilot-scale tests were conducted of alkylation catalysts based on domestic carriers. The reactor was a hollow cylindrical apparatus with a volume of 130 dm<sup>3</sup> and an inside diameter of 250 mm. It was equipped with a heating jacket and measuring equipment. The catalyst was made in the reactor itself by saturating dewatered carrier with boron trifluoride. Catalysts based on SKTB carrier had significantly lower activities and stabilities than did the imported catalysts, which was apparently due to their small average pore radius. A-64M catalyst was superior to SKTB and equal to the imported catalyst. Figure 1, references 2: 1 Russian, 1 Western.

UDC 541.128:541.124:542.943:547.21+577.15:577.352

### Mechanism and Selectivity in Biological Oxidation of Alkanes

18410152a Moscow KINETIKA I KATALIZ in Russian  
Vol 30 No 1, Jan 89 (manuscript received  
19 Nov 87) pp 7-20

[Article by A. M. Khenkin and A. A. Shteynman, Division of the Institute of Chemical Physics, USSR Academy of Sciences, Chernogolovka]

[Abstract] Analysis of published experimental data was presented on the oxidation of alkanes in enzymatic reactions and in chemical models. An attempt was made to elucidate the mechanism of these processes and to discuss the concepts of their unique and highly selective actions. This review covers the following aspects: basic principles of enzymatic oxidation of alkanes; nature of the active oxidizer, and the mechanism of its interaction with alkanes. Based on these data, it was shown to be possible to get a chemical model for cytochrome P-450

based on ferroporphyrines which are as good as the enzymatic systems for hydroxylation of alkanes. By changing the porphyrine structure and its microsurroundings, or by altering the solid support, the regional selectivity of the oxidation of linear alkanes could be changed significantly. A mechanism was proposed for alkane oxidation by P-450 cytochrome and the reasons for the unusual selectivity in biooxidation of alkanes were presented. References 59: 17 Russian, 42 Western (10 by Russian authors).

UDC 541.127:541.117:[547.263+546.264]\*

### Kinetics and Mechanism of Action of Low Temperature Phosgene Reaction With Isopropyl Alcohol

18410152b Moscow KINETIKA I KATALIZ in Russian  
Vol 30 No 1, Jan 89 (manuscript received  
27 Jan 88) pp 55-62

[Article by L. N. Margolin, A. L. Sidelkovskiy, A. F. Vasilyev, T. I. Bondareva, M. B. Stepanov, and G. B. Sergeyev, All Union Scientific Research Institute of Chemical Plant Protective Agents, Moscow; Moscow Institute of Chemical Machinery Construction; Department of Chemistry, Moscow State University imeni M. V. Lomonosov]

[Abstract] Studying the effects of complex formation and of the accumulating reaction products on the kinetics and mechanism of phosgenation of alcohols, the kinetics of phosgene reaction with isopropyl alcohol was investigated in the temperature range 183-283 K using combined diffraction spectroscopy and varying the reagents ratio from 1 to 12. Four distinct kinetic regions of this reaction were observed differing by the temperature level and the degree of isopropyl alcohol conversion. Only in the last region (temperature above 263 K) did the reaction go to completion; in the first three ( $T = > 193, 213 \geq T \geq 233, 238 \geq T \geq 258$  K) it was arrested when unreacted reagents were still present. This slow-down was due to a complex formation between isopropyl alcohol and HC1, one of the reaction products [ $HC1.(iso-C_3H_7OH)_n$ , where  $n = 1$  to 3]. This "kinetic process arrest" appeared to be general for reactions using high concentration of reagents and low temperatures: phosgenation of alcohols and primary amines, reaction of alcohols with alkylchloroformate, etc. Figures 4; references 9: 6 Russian, 3 Western.

UDC 541.127:546.41-31'264:532.785'787+628.165

### pH Effect on Kinetics of Mass Crystallization of Calcium Carbonate

18410152c Moscow KINETIKA I KATALIZ in Russian  
Vol 30 No 1, Jan 89 (manuscript received  
15 Oct 87) pp 78-82

[Article by M. A. Kamkha, P. B. Sibiryakov and V. L. Biziayev, Institute of Chemical Kinetics and Combustion, Siberian Division of USSR Academy of Sciences, Novosibirsk]

[Abstract] The goal of this work was to provide quantitative description of the kinetics of calcium carbonate

precipitation, specifically concentrating on the effect of pH ( $\text{HCO}_3^-$ ) on this process. It was shown that the hydrocarbonate anion plays a determining role in precipitation of calcium carbonate, especially at pH below 9. A similar effect could be observed also in other polybasic acid precipitation (sulfates, phosphates). The principal thermodynamic factor determining the initiation of  $\text{CaCO}_3$  precipitation in all cases is the relative supersaturation which is pH independent and at 400 degrees C amounts to about 45. It was shown that in the initial stage of the reaction, the area of effective specific surface of the dispersed phase grows linearly, i.e. at  $\tau_{\max} \cdot s_{\max} = \text{const}$ . The surface is independent of  $\text{Sup}_0$  and pH up to  $\text{Sup}_{\max} = 150$ . Figures 4; references 15: 8 Russian (2 by Western authors), 7 Western.

UDC 542.973:541.124-145:546.98'141-386:  
541.634:547.314.2:542.951

### Some Aspects of Catalyst Formation Mechanism for Carbalkoxylation of Acetylene in $\text{PdBr}_2\text{-P(OPh)}_3\text{-nBuOH}$ System

18410152d Moscow KINETIKA I KATALIZ in Russian  
Vol 30 No 1, Jan 89 (manuscript received 22 Oct 84,  
after final revision 1 Sep 87) pp 98-105

[Article by N. G. Mekhryakova, A. N. Nyrkova, N. F. Alekseyeva, G. M. Shchulyakovskiy and O. N. Temkin, Saratov Branch of Scientific Research Institute of Chemistry and Technology of Polymers imeni V. A. Kargin and Moscow Institute of Fine Chemical Technology imeni M. V. Lomonosov]

[Abstract] Investigation of the formation of active catalysts for carbalkoxylation of methylene in the system  $\text{PdBr}_2\text{-P(OPh)}_3\text{-nBuOH}$  showed that the process occurs in three phases. First, when  $\text{PdBr}_2$  is dissolved in the solution, only two complexes are formed:  $\text{PdBr}_3^-$  (35 percent) and  $\text{PdBr}_4^{2-}$  (65 percent). Small quantities of water ( $\text{H}_2\text{O}$ ) with  $\text{Br}^-$  in butanol. At the second stage, when triphenylphosphite is added, an insoluble complex  $\text{cis-PdL}_2\text{Br}_2$  is dissolved in mother liquor at 70-100 degrees, a mixture of  $\text{cis-Pd[P(OPh)}_n(\text{OBu})_{3-n}]_2\text{Br}_2$  is formed in presence of  $\text{H}^+$  in which L is 20-60 percent transesterified. In the "anhydrous" solution, the transesterification reaches the level of 70-95 percent, but the mixture is inactive as a catalyst. This cis complex appears to be active because of the presence of two trans-coordinates L-Pd-Br which facilitate formation of the complexes  $\text{L}_2\text{PdBr}(\text{OR})$ ,  $\text{L}_2\text{PdBr}(\text{CO})^+$  and  $\text{L}_2\text{PdBr}(\text{COOR})$ . Figures 2; references 22: 21 Russian (2 by Western authors), 1 Western.

UDC 541.128:541.127:542.943.6:547.563.024:  
547.553:541.636

### Reaction of Sterically Hindered Aroxyl Radical with Hydroperoxide Catalyzed with Aromatic Amines

18410152e Moscow KINETIKA I KATALIZ in Russian  
Vol 30 No 1, Jan 89 (manuscript received  
16 Nov 87) pp 106-111

[Article by V. T. Varlamov and Ye. T. Denisov, Division of Institute of Chemical Physics, USSR Academy of Sciences, Chernogolovka]

[Abstract] Aromatic amines participate actively in splitting off hydrogen atoms with peroxide radicals, indicating at

least principal possibilities for molecular-radical catalysis of these slow radical reactions. Recently this type of catalysis was reported in the reaction of 2,4,6-tri-tert-butylphenoxy with hydroperoxide. In continuation of such work, in the present paper the kinetic scheme of this catalytic reaction was analyzed, conditions were formulated at which such catalysis is possible and kinetic study was carried out on the basis of the reaction of a stable radical 2,4,6-tri-tert-butylphenoxy with cumyl hydroperoxide catalyzed by three substituted diphenylamines. It was shown that the catalysis was the result of the raid reaction of  $\text{ArO}^\bullet$  with  $\text{AmH}$  and high activity of aminyl radicals  $\text{Am}^\bullet$  in reactions splitting the H atom from  $\text{ArOH}$  and  $\text{ROOH}$ . The constants  $K_3K_4$  were found to be 36.85, 5.93 and 5.53 1/mole's for 4,4'-dimethoxy-, 4,4'-dimethyl- and 4,4'-di-tert-butylidiphenyl-amines, respectively. Figures: 2; references: 10 (Russian).

UDC 541.128.13:541.124-145.4:542.955:  
[547.538.141+547.539.4]:546. 98'26

### Kinetics of Styrene Arylation with Substituted Benzene Iodides in Presence of Palladium on Charcoal

18410152f Moscow KINETIKA I KATALIZ in Russian  
Vol 30 No 1, Jan 89 (manuscript received  
5 Jan 88) pp 138-141

[Article by T. A. Sarycheva, A. N.I Novikova, and A. K. Yatsimirskiy, Tomsk Polytechnical Institute; Department of Chemistry, Moscow State University imeni M. V. Lomonosov]

[Abstract] Arylation of olefines with aryl iodides in presence of  $\text{Pd}(\text{OAc})_2$  and  $\text{R}_3\text{N}$  is a convenient method of producing 1,2-diarylethylenes. This process occurs also in presence of  $\text{Pd/C}$  and  $\text{Bu}_3\text{N}$  in DMFA. Kinetics of this arylation was investigated on styrene and benzene iodide. The reaction went smoothly at 100-130 degrees. The stationary reaction rate was found to be directly proportional to the concentration of catalytically active Pd form. The role of  $\text{Bu}_3\text{N}$  was to neutralize the HI formed during the reaction and to accelerate the reaction rate. Kinetic equation was derived corresponding to the expressed reaction mechanism; it includes a sequence of reversible reactions of the catalyst with each reagent. Following three steps represent the reaction mechanism: oxidative addition of aryl iodide to Pd (0), addition of olefine along the aryl-palladium bond and  $\beta$ -elimination of palladium hydride which breaks down rapidly to  $\text{Pd(O)}$  and HI. Figures 2; references 9: 4 Russian (all by Western authors), 5 Western (1 by Russian authors).

UDC 541.128.3:547.211:546.46'623:542.943'952

### Effect of Composition of $\text{MgO}$ Based Catalysts on Their Activity in Oxidative Conversion of Methane

18410152g Moscow KINETIKA I KATALIZ in Russian  
Vol 30 No 1, Jan 89 (manuscript received  
2 Jun 87) pp 142-147

[Article by N. P. Kirik, V. G. Roguleva, N. G. Maksimov, A. S. Ivanova, V. Ye. Volkov, and A. G. Anshits, Institute of Chemistry and Chemical Technology, Siberian Division of USSR Academy of Sciences, Krasnoy-

arsk, and Institute of Catalysis, Siberian Division, USSR  
Academy of Sciences, Novosibirsk]

[Abstract] Catalytic and physical-chemical properties of complex systems based on MgO were investigated in the reaction of oxidative conversion of methane at 900-1050 K. It was shown that with different composition of the catalysts the mechanism of the formation of carbon dioxide differed: formation of C<sub>2</sub>-hydrocarbons and CO<sub>2</sub>

occurs by a sequential-parallel or by sequential scheme. CO formation occurs through conversion of methane with strongly adsorbed water or by decomposition of surface methoxyl ions. Increase in crystallinity of aluminum-magnesium catalysts leads to lower activity during deep methane oxidation. A correlation was noted between the catalytic activity and concentration of defects in MgO structure stabilized with Fe<sup>3+</sup>. Figures 3; references 15: 5 Russian, 10 Western.

UDC 676.164.085.2.065:665.948.1

### Fractional Distillation of Sulfate Turpentine Raw Material

*18410113d Moscow GIDROLIZNAYA I LESOKHIMICHESKAYA PROMYSHLENNOST in Russian No 7, Oct-Nov 88 pp 22-23*

[Article by N. P. Khmelev, senior engineer, Gorkiy Specialized Administration "Leskhimmontazhnaladka," S. I. Korostelev, chemical shop chief, and M. I. Selyuzhitskiy, production engineer, "Pitkyaranta" Cellulose Plant]

[Abstract] Fractional distillation of sulfate turpentine has been put online at the "Pitkyaranta" Cellulose Plant. Prestart operations revealed a number of problems in the process. These were corrected, thereby reducing the quantity of irrecoverable head fraction to 2.5 percent of the mass of raw material charged as opposed to 8-10 percent according to the original plan. Major changes included replacing steam at 0.4 MPa with steam at 1 MPa, decreasing energy consumption per ton of product produced, and reducing consumption of the raw material from 1.255 to 1.15 per ton of end product. Figure 1.

UDC [661.7:547.415.1].002.237

### Improving Evaporation of Amines and Crystallization of Common Salt

*18410120A Moscow KHIMICHESKAYA PROMYSHLENNOST in Russian No 10 Oct 88 pp 592-593*

[Article by R. N. Zagidullin]

[Abstract] The evaporation of ammonia and the crystallization of common salt in the production of polyethylene polyamines are frequently accompanied by clogging of the crystallizers. It has been shown that treatment of a salt solution from an evaporator with 33-45 percent alkali can yield significant quantities of amines. The still product of evaporation equipment contains valuable bases. Chemical analysis methods and gas-liquid chromatography were used to determine the composition of the amines and salt present. The degree of extraction of

amines was studied as a function of alkali concentration, settling time, and temperature. As the alkali concentration was increased, the degree of extraction of amines increased from 4 to 76 percent. As the settling time was increased to 20 minutes, the extraction of amines from the mother liquor increased; however, further time increases did not result in any increase in the extraction. Increasing the settling temperature from 40-80°C with 45 percent NaOH 1:1 by volume decreased the extraction of amines. A process has been developed on the basis of these results for optimum extraction of amines. Figure 1, references 5: 2 Russian, 1 Polish, 2 Western.

UDC 661.418.1

### Electrolysis of Sodium Chloride Solution With Polymer Diaphragms

*18410120D Moscow KHIMICHESKAYA PROMYSHLENNOST in Russian No 10 Oct 88 pp 609-610*

[Article by A. F. Mazanko, V. V. Bannikov, V. B. Vorobeva, I. A. Ivanter, A. T. Pylayeva, and V. S. Bobrin]

[Abstract] A study was made of the influence of current density and polymer diaphragm thickness on electrolysis characteristics in the production of chlorine and caustic soda so as to determine the maximum concentration of the sodium hydroxide solution produced while retaining high yield per unit of current. Tests were performed in an electrolyzer with horizontal electrodes and a polymer diaphragm. A sodium chloride solution with a concentration of 305 g/dm<sup>3</sup> was processed at 90°C by using a diaphragm manufactured by rolling a mixture containing polytetrafluoroethylene, a pour-former, and a wetting agent. The increase in sodium chlorate concentration in the electrolyte, in contrast to asbestos-containing diaphragms, occurs before the limiting concentration of sodium hydroxide is reached. Sodium hydroxide solutions with a broad concentration range (72-160 g/dm<sup>3</sup>) can be reached with a high yield per current, 96-98 percent. It is best to operate at the maximum possible sodium hydroxide concentration by using a sodium chloride solution acidified with hydrochloric acid to reduce the sodium chlorate concentration. Figures 3, references 13: 11 Russian, 2 Western.

### Electrochemical Generators—Power Source of the Future

18410146a Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 10 Feb 89 p 3

[Article by V. Lapikura, senior research associate, Institute of World Economics and International Relations, USSR Academy of Sciences: "Electricity ... From the Air"; first paragraph is article introduction in source]

[Text] *"Without electrochemical generators it would have been much more complicated to land a man on the Moon," American specialists feel. "Such devices will be even more necessary to produce electricity in future exploration of space: on manned flights to Mars and in the establishment of permanent stations on the other side of the Moon."*

What is this miracle source that has drawn the attention of today's scientists and engineers, not only those involved in space research, but also many who work in "terrestrial" professions: auto makers, ecologists and power engineers?

Before answering this question, let us remind the reader that mankind obtains about 95 percent of its primary energy needs by transforming in some way or other the chemical energy contained in organic sources—coal, gas and petroleum. In the process, more than half this energy is lost forever. Water and air become polluted. Heat and electric power stations are a typical example.

A logical question arises: how to avoid losses? One of the possible means proposed by scientists is to produce electric power by direct conversion of the chemical energy of fuel into electric power, bypassing the thermal form, which means excessive loss is ruled out. It is possible to obtain such conversion in electrochemical generators (ECG), which also "know how" to operate with the most unusual types of fuel. In simplified form, the principle of ECG operation is comparable to a battery (it is also a galvanic cell); but because of the special catalysts in it, hydrogen and alcohols, aldehyde and natural gas, diverse products of petroleum and coal refining, and even metals—such as zinc or magnesium—can be used as the active material for the negative electrode. Oxidizing agents such as atmospheric oxygen or chlorine are generally used in the role of positive electrode.

The fuel and oxidizing agent are stored separately and delivered to generator electrodes gradually and continuously. The ECG operates as long as there is delivery of active substances into the unit where the oxidation reaction takes place. This distinguishes it appreciably from batteries, in which electrodes contain only a certain amount of active materials. After the battery's depletion, they lose their efficiency and require recharging.

According to published data, it has not yet been possible to prevent all losses of energy, and for this reason the efficiency of the ECGs that have been developed ranges from 60 to 80 percent, although theoretically it could come very close to 100 percent. But even these achievements enable

an electric vehicle equipped with electrochemical generators to travel twice as far as a car with an internal combustion engine with the same fuel consumption.

In addition to the foregoing, we should mention several advantages of ECGs: their ecological purity, self-contained operation, absence of noise, resistance to overloads and short circuits, wide range of choice of available and inexpensive fuels, and generation of direct current. All this advances electrochemical generators to the ranks of energy sources of the future, with the help of which it will be possible to explore space, remote arctic and antarctic regions, and the expanses of Siberia and the Far East.

When an ECG, instead of an engine, is installed in a motor vehicle, it is no longer necessary to have a metering system for fuel, ignition, or lubrication. It will no longer have the usual gear box and assemblies of transmission systems that are growing increasingly complicated. U.S. specialists from the Los Alamos National Laboratory have already developed an ECG for use as the power plant for city buses. Methanol and atmospheric oxygen will be used as fuel for such an environmentally safe means of transportation. An experimental tractor and a motor vehicle operating on ECGs have already been discussed in the foreign press. The same energy sources are used in small radio stations and noise-free early warning radar units, the average operating time of which is 1500-2000 hours and, in some cases, up to 2 years. There are also plans to develop power plants for compact cars.

The intensive research and work that has been done for more than 20 years in the United States, Japan, England, France, FRG and several other countries have made it possible already to turn to development of large-scale power installations on an industrial level. For example, the American-Japanese concern called International Fuel Cells has developed a unit capable of producing 11,000 kW power. The first deliveries are being made this year on orders for 23 such ECGs. In the meantime, demonstration installations are operating successfully in New York and Tokyo.

Of course, the cost of electric power generated by ECGs is still rather high, although it is comparable to traditional energy sources: according to existing estimates it is 30-70 percent higher. However, scientists and specialists are quite optimistic. They believe that work done recently on improving the efficiency of ECGs and lowering the costs of materials, as well as the reduction of production expenses when mass production is begun, will make it possible to substantially lower the cost of "electrochemical" energy in the near future. But there is still a wealth of work ahead of us.

Improvement of fuel cells is proceeding more successfully in the United States than anywhere else. Power installations capable of producing a total of 6 million kW of power are expected to be in operation there by the year 2003; by the year 2008, the figure is expected to be 14 million. Work is also in progress in the Soviet Union. As far back as 1961, we produced a laboratory prototype of an electrochemical generator with efficiency in excess of 65 percent. However, it is too soon to discuss mass-scale introduction of

this promising source of energy. But it is quite obvious that ECGs will play an important part in conserving energy and solving ecological problems.

UDC 543.257:541.49:546.47

**Complex Compounds of Quinoxaline-2,3-Dithiol With Zinc as Ion-Active Membrane Electrode Substances**  
*18410111d Kiev UKRAINSKIY KHMICHESKIY ZHURNAL in Russian Vol 54 No 11, Nov 88 (manuscript received 2 Jun 87) pp 1172-1176*

[Article by O. P. Ryabushko, A. T. Pilipenko, L. A. Batkovskaya, and Yu. S. Savin, Kiev University]

[Abstract] Complex compounds of quinoxaline-2,3-dithiol with ions of zinc, cadmium, mercury, copper, silver, nickel, cobalt, lead, palladium, and a number of other

metals were studied. Isolated as a solid sediment or extract, these chelates were impregnated into matrices of carbon-graphite paste or polyvinyl chloride film. Quinoxaline-2,3-dithiol interacts with bivalent metal ions to form complex compounds with a metal:reagent ratio of 1:2. The reagent and its chelates are insoluble in water, dilute acids, and chloroform but soluble in alkalis, ammonium hydroxide, alcohols, DMFA, and DMSO. Zinc-selective paste electrodes were manufactured out of spectral carbon-graphite powder with paraffin-containing salts and chelates of metals with organic reagents to demonstrate the correctness of the use of carbon materials as the matrix. Studies of membrane electrodes based on complex zinc compounds with quinoxaline-2,3-dithiol showed the suitability of their use for direct potentiometric measurements and also for potentiometric titration. Figures 2, references 9: Russian.

**Ecological and Economic Impact of Improvements  
in Plastics Production**  
*18410146b Moscow SOTSIALISTICHESKAYA  
INDUSTRIYA in Russian 25 Feb 89 p 1*

[Article by Academician B. Laskorin and Professor A. Novikov, doctor of engineering sciences, under the rubric "Competition for Prize of USSR Council of Ministers": "In Alliance With Ecology"]

[Text] We live in a world of polymers, which have become irreplaceable attributes of our times. But people who happily use plastic products do not want to live next to the plants that produce plastics. The business is far from harmless, and it is technologically complicated and devours much scarce raw material.

How then can we introduce in plastics production what seems impossible to introduce there—great economy, normal working conditions and environmental safety? Attempting to answer that question has been a team of authors from among the specialists at the Moscow Scientific Production Association Plastik, the Gosplastproyekt Institute in Rostov-on-Don, the Ukrainian Academy of Sciences Kiev Institute of Physical Chemistry imeni L. Pisarzhevskiy, the Ukrainian Scientific Research Institute of Plastics Machine Tools of the Bolshevik Scientific Production Association, and the All-Union Scientific Research Institute of Labor Safety of the All-Union Central Council of Trade Unions in Leningrad. Testing of the set of developments they proposed for radically improving plastics production was performed at the Vilnius Plasta plant.

It was expressly the breadth of the search and the combined approach that helped the authors avoid the mistakes that are inevitable when research is pursued in separate directions. It most certainly could not have been otherwise: after all, all factors are intertwined in a complicated skein at chemical plants. It is difficult to reconcile, for example, the requirements of technological feasibility, conservation of resources and environmental protection by trying to pull out only one strand.

Science has not yet uttered its last word, while the solutions it has proposed are already being introduced at the existing Plasta plant. What has this offered to the enterprise? In brief, there has been a radical reconstruction there, and plastics processing has advanced to a qualitatively new level.

Special mention should be made of the first-ever development in our country of a catalytic neutralizing system that makes it possible to remove up to 95% of the phenol and formaldehyde from low-concentration emissions into the ventilation system. Adoption of a closed-loop automated system of water supply, which makes it possible to abandon the diversion of water from natural

sources or the water pipeline systems, merits all sorts of praise in our time of ecological crisis. Accordingly, this precludes the dumping of industrial waste into open water reservoirs.

The technology and equipment introduced for high-volume production of polyethylene film are also among the pioneering innovations. They involve the use of a basically new system of automatic monitoring of thickness and size, which saves a considerable amount of raw materials. In this area of development, the waste-free technology for processing thermoplastics is of great interest. With the help of the collaborators, the people of Vilnius were the first in the country to adopt production of polyethylene pipes for gas-distribution networks made of domestic composite raw materials.

Introduction of all these measures is enabling the Plasta plant to save annually more than 300 tons of polymers and 2.5 million cubic meters of potable water and to lower by 5 percent the consumption of heat and electric power. Unfortunately, we still have no clear-cut methods to assess the impact in terms of the reduction of environmental pollution. But it is felt that just the elimination of harmful releases or the use of by-products yields a gain that at least covers expenses.

The publication, "Development and Introduction of a Set of Highly Efficient Scientific-and-Technical Designs Aimed at Accelerating the Socioeconomic Development of Plastics Production," has enriched us also with the know-how of an alliance of scientists and production workers that can be put to good use not only in the chemical industry, but also in other sectors. In particular, in the course of adopting the innovative solutions, more than 100 enterprises have already followed the example of the Plasta plant. All this allows us to add our voice to those who believe that the creative team of innovators deserve the prize of the USSR Council of Ministers.

UDC 628.543.56:[661.7:547.466.2]

**Biochemical Purification of Wastewater  
Containing Higher Fatty Acids and Their Amino  
Derivatives**  
*18410087c Moscow KHIMICHESKAYA  
PROMYSHLENOST in Russian  
No 11, Nov 88 pp 679-680*

[Article by O. I. Dosmaylova, L. A. Mukhina, A. I. Mazyrina, and D. N. Pankov]

[Abstract] A study is made of biochemical oxidation of wastewater from the production of acylated amino acids by active silt in order to determine its adaptation, optimal process parameters, and degree of purification. Studies were performed on a laboratory model of an aerated mixing tank with a volume of 3.2 dm<sup>3</sup> and air input of 39 m<sup>3</sup>/m<sup>3</sup>. After a month of adaptation, the active silt stabilized at 2.4 g/l, with a silt index of 91

mg/g. The silt became dense and settled well. The biocenosis consisted predominately of *Monostyla cornuta*, *Philodina roseola*, plus *Vorticella campanula* with many *Carchesium* colonies, *Aspidisca costata*, and *Stylonychia mytilus*. In 2 weeks of operation under these conditions, 90-98 percent purification was achieved. The optimal pH was found to be 9, which was achieved by adding 1 N NaOH solution to the incoming water. References 8: 6 Russian, 2 Western.

UDC 630\*86:628.543

#### Purification of Wastewater in Ponds

18410113b Moscow *GIDROLIZNAYA I LESOKHIMICHESKAYA PROMYSHLENNOST* in Russian No 7, Oct-Nov 88 pp 18-19

[Article by L. I. Kornilov, Ye. M. Kryuchikhin, Specialized Prestart Environmental Protection Administration, All-Union Scientific Production Association of the Paper and Pulp Industry, and A. I. Lavrov, chief, Purification Structures Shop, Neyvo-Rudyanskiy Wood-Chemical Plant]

[Abstract] Wastewaters from the authors' chemical plant are treated in two rectangular aeration ponds with a total volume of 25,000 m<sup>3</sup>, a depth of 3 m, with settling and aeration zones separated from each other by longitudinal watertight concrete walls. The water flows through the ponds in a total of 5 days, decreasing the content of suspended matter to 8 g/m<sup>3</sup>, the organic matter content to 8 g/m<sup>3</sup> based on BOD<sub>20</sub>, and the oxygen content to 8 g/m<sup>3</sup>. However, it was not anticipated that the surface of the water would freeze over in winter and thereby

prevent the water from traveling through the system. To prevent the aeration tanks from being broken by the ice, they were removed from the pond in the winter. It was found that even with the aeration tanks removed natural aeration in the winter in the northern climatic zone was sufficient to purify the water. Water falling over concrete separators in streams achieved sufficient oxygen content in the winter. The new technology does not require any adjustment or servicing when operated in the winter. References 4: Russian.

UDC 676.164.085:504.06

#### Gas Purification Device

18410113c Moscow *GIDROLIZNAYA I LESOKHIMICHESKAYA PROMYSHLENNOST* in Russian No 7, Oct-Nov 88 pp 20

[Article by N. V. Vrotushina, production engineer, evaporator shop, Baykal Paper and Pulp Combine]

[Abstract] A rotoclone was installed in the author's shop to improve the effectiveness of gas purification to remove sulfur compounds. The device is a rectangular container made of stainless steel measuring 660×1,820×366 mm, within which are valves and barriers to regulate the gas flow speed and an alkali level regulator. Drop liquids from the gases are trapped by a labyrinth. Gases are driven from the reactor to the rotoclone by a 3,000 m<sup>3</sup>/h fan. The sulfur-containing gases contact the white alkali contained in the rotoclone, which absorbs the sulfur compounds and decreases their concentration. The white alkali is periodically replaced as it is exhausted.

UDC 66.099.2

**Production of Carbamide Macrogranules With and Without Coatings**

*18410085c Kiev KHIMICHESKAYA TEKHNOLOGIYA: NAUCHNO-PROIZVODSTVENNYY SBORNIK in Russian No 6, Nov-Dec 88 (manuscript received 28 Sep 87) pp 20-22*

[Article by E. A. Karpovich, B. G. Kholin, N. P. Kononenko, and S. V. Vakal, Sumy Affiliate, Kharkov Polytechnical Institute]

[Abstract] The expediency of producing fertilizers in macrogranular form with and without coatings to retard dissolution is studied. It is found that without changing the existing technology of carbamide granulation in towers modernization of the melt vibrogranulator can achieve granulated carbamide with 2- to 4-mm grain size instead of the usual 1-2.5 mm. A pilot-scale model of such a granulator has been tested and installed at one of the plants in the nitrogen fertilizer industry. Studies have now been continued on the manufacture of larger granules, up to 15 mm in size, by using an installation with a plate-type granulator. The granules can be coated in the pelletizing equipment to slow dissolution. A cross-sectional photograph is shown of a coated granule, including a transition

zone between the granule and the coating, which helps to increase its strength. The 5- to 8-mm granule-size fraction is considered most promising. Figures 3, references 3: Russian.

UDC 661.635.223.001.5

**Intensification of Nitroammophosphate Technology**

*18410120c Moscow KHIMICHESKAYA PROMYSHLENNOST in Russian No 10, Oct 88 pp 599-603*

[Article by V. N. Kochetkov, A. V. Gal'tsov, Ye. V. Tulina, and Ye. V. Ilina]

[Abstract] A mathematical description of the process of nitroammophosphate manufacture was developed in order to determine optimal manufacturing conditions. Studies were performed on the manufacture of a broad assortment of fertilizers with varying  $P_2O_5$  contents,  $NH_3$ :  $H_3PO_4$  ratios, and water contents. The studies indicated that it is undesirable to use  $H_2SO_4$  as an absorbent in nitroammophosphate manufacture since this requires an excess quantity of water and an increase in the recirculation factor, which result in losses of ammonia, tackiness of the product, and a reduction in the volume of complex fertilizer produced. Sulfuric acid should be used only when nitroammophosphates with a molar  $NH_3$ :  $H_3PO_4$  ratio of 1.05-1.10 are manufactured; this requires about 5 kg  $H_2SO_4$  per ton of product. In manufacturing this product, increasing  $SO_3$  from 0 to 5 percent increases the temperature of the slurry to 141.5°C, decreases the recirculation factor to 1.9, and reduces the moisture content of the mixture leaving the reactor to 1.2 percent. Figure 1.

UDC 546.17:539.213

**Chalcogenide Glasses Containing Chemically Bonded Nitrogen**

18410086a Riga IZVESTIYA AKADEMII NAUK LATVIYSKOY SSR: SERIYA KHIMICHESKAYA in Russian No 5, Sep-Oct 88 (manuscript received 13 Nov 87) pp 536-540

[Article by M. B. Raytsis, L. S. Raytsis, and M. B. Tiltinsh, Institute of Inorganic Chemistry, Latvian Academy of Sciences]

[Abstract] A study is made of certain properties of vitreous chalcogenide compositions containing chemically bonded nitrogen. Specimens were synthesized in high-frequency and pulsed nitrogen discharges from mechanical mixtures of three to five of the following elements: tellurium, gallium, germanium, silicon, phosphorus, and aluminum. The probability of the formation of chemical bonds in such compositions is determined not only by the bond energy but also by the frequency of occurrence of various atoms in the composition, discharge parameters, and the conditions under which the synthesis product is precipitated. Figures 6; references: 4 Russian; 1 Western.

UDC 666.113'821'662'289'28'18

**Formation of Crystalline Phases in CdO-RO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub>(R=Si, Ti, Ge) Compositions Depending on Temperature**

18410086b Riga IZVESTIYA AKADEMII NAUK LATVIYSKOY SSR: SERIYA KHIMICHESKAYA in Russian No 5, Sep-Oct 88 (manuscript received 17 Oct 87) pp 541-542

[Article by A. Ya. Ilgatse and Ya. Ya. Bolshiy, Riga Polytechnical Institute imeni A. Ya. Pelshe]

[Abstract] The formation of crystalline phases is studied in compositions in the system CdO-RO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub>, where R is Si, Ti, or Ge. Compositions on the RO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> side of the concentration triangle are also studied. These have the characteristic retention of the calculated content of system components after glass making. X-ray phase analysis indicates that the first crystalline phases are silicon, titanium, and germanium phosphates. As the content of CdO increases, phosphates of cadmium are formed. Finally, maxima appear on the diffraction diagrams that correspond to unreacted CdO. Compositions

containing titanium and germanium dioxides become x-ray amorphous at comparatively lower processing temperatures. Figure 1, references 6: 5 Russian, 1 Western.

UDC 666.016.2:512.96

**Computer Search for Optimal Multicomponent Silicate Glass Compositions**

18410086c Riga IZVESTIYA AKADEMII NAUK LATVIYSKOY SSR: SERIYA KHIMICHESKAYA in Russian No 5, Sep-Oct 88 (manuscript received 16 Sep 87) pp 543-546

[Article by V. M. Kozyukov and T. I. Kozyukova, Riga Polytechnical Institute imeni A. Ya. Pelshe]

[Abstract] A computer search is conducted for optimal glass compositions by varying the polyhedron studied within the limits of an individual system and increasing the number of criteria from 2 to 8 and the number of components from 3 to 6. The influence of changing the dimensions of the search area on the results of vector optimization is studied by way of the example of glasses in the system Na<sub>2</sub>O-SrO-PbO-SiO<sub>2</sub>, with the limits of the molar content of the components increased from 10 to 30 at intervals of 5 percent. The system can compare optimal compositions of glasses found in different systems. The dimensions of the search polyhedron and the number of criteria used do not influence the accuracy of the search for optimal glass compositions. Accuracy does decrease with an increase in the number of components, although the maximum error does not exceed 0.5 molecular percent for a six-component system. References 8: Russian.

UDC 541.12.034

**High Pressures—New Prospects for Solid-State Chemistry**

18410094a Moscow ZHURNAL NEORGANICHESKOY KHIMII in Russian Vol 34 No 1, Jan 89 (manuscript received 9 Mar 88) pp 3-11

[Article by Zh. Demazo, P. B. Fabrichnyy, V. A. Legasov, deceased, Zh. Eturno, and P. Khagenmyuller, Laboratory of Solid State Chemistry, National Scientific Research Center, France; Moscow State University imeni M. V. Lomonosov]

[Abstract] This article reviews the use of high pressures for solid-state synthesis, production of new materials, and structural transformations. High-pressure methods represent an effective tool for solid-state chemistry, which is of significant interest both for basic research (to achieve a better understanding of the relationship between chemical composition, crystalline structure, and physical properties) and for applied research (as in the

production of chromium dioxide powders for magnetic recording, synthesis of diamonds and cubic boron nitride for technological purposes, and passivation of semiconductor elements for microelectronics). The development of high-pressure technology is closely related to progress in modern materials science and the development of new methods of physical and chemical diagnosis. Figures 6, references 36: 2 Russian, 34 Western.

UDC 546

**Complex  $\text{Ln}_2\text{Fe}_{2/3}\text{Mo}_{4/3}\text{O}_7$  Oxides With Pyrochlore-like Structure**

18410094b Moscow ZHURNAL NEORGANICHESKOY KHIMII in Russian Vol 34 No 1, Jan 89 (manuscript received 10 Dec 87) pp 23-26

[Article by G. V. Bazuyev, O. V. Makarova, and N. A. Kirsanov, Institute of Chemistry, Urals Division, USSR Academy of Sciences, Sverdlovsk]

[Abstract] Data are presented on the synthesis and certain properties of the complex oxides  $\text{Ln}_2\text{Fe}_{2/3}\text{Mo}_{4/3}\text{O}_7$ . The compounds were synthesized at  $1.3 \cdot 10^{-3}$  Pa in a tungsten-heated furnace at  $1,300^\circ\text{C}$  for 36 hours. X-ray diffraction studies and measurements of magnetic susceptibility were performed. The results indicated that the degree of oxidation of d elements corresponds to the formula  $\text{Ln}_2\text{Fe}_{2/3}^{3+}\text{Mo}_{2/3}^{5+}\text{Mo}_{2/3}^{4+}\text{O}_7$ . Figures 3, references 9: 3 Russian, 6 Western.

UDC 535.379:541.127:539.186:  
[546.28+546.295'161].024

**Cheiluminescence and Formation of Electron-Excited Radicals in Reaction of Si With  $\text{XeF}_2$**

18410110a Moscow KINETIKA I KATALIZ in Russian Vol 29 No 5 Sep-Oct 88 (manuscript received 26 Sep 86) pp 1031-1037

[Article by M. R. Baklanov, I. A. Badmayeva, and K. P. Mogilnikov, Institute of Semiconductor Physics, Siberian Division, USSR Academy of Sciences, Novosibirsk]

[Abstract] A study is made of the chemiluminescence spectrum in the visible area as Si reacts with  $\text{XeF}_2$  and its sources are identified. The formation mechanism of electron-excited radicals responsible for the chemiluminescence is studied. Kinetic experiments were performed in a vacuum chamber at  $10^{-5}$ - $10^{-6}$  mmHg. The results indicate that primary formation of radicals occurs with an  $\text{XeF}_2$  deficit, at the moment when the  $\text{XeF}_2$  feed is started and around the parameter of the beam. Chemiluminescence results from the formation of electron-excited  $\text{SiF}_2$  and  $\text{SiF}_3$  radicals as a result of a gas-phase reaction of lower silicon fluorides desorbed from the surface with  $\text{XeF}_2$ . The reactions also lead to the formation of F atoms, increasing reactivity of the system for  $\text{SiO}_2$ . The kinetics of chemiluminescence and the ratio of the reaction products are largely determined by the parameters of the absorption layer. Preferential desorption of lower fluorides is possible only with lower degrees of filling of the second adsorption layer of  $\text{XeF}_2$  on the surface of the Si. A decrease in the concentration of lower fluorides in the gas phase increases the effective flow of  $\text{XeF}_2$  to the surface of the Si, and the adsorption extinction of chemiluminescence becomes autocatalytic in nature. Figures 3, references 14: 3 Russian, 11 Western.

UDC 546.65'821+548.734

**Double Rare Earth Oxides  $\text{Ln}_2\text{TiO}_5$**   
*18410111a Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 54 No 11, Nov 88 (manuscript received 10 Jun 87) pp 1127-1129*

[Article by S. A. Nedilko and Ye. G. Zenkovich, Kiev University]

[Abstract] Considering that rare earth titanates and materials based upon them are widely used in electronic, laser, and nuclear technology, the authors studied processes of the formation of compounds with the structure  $\text{Ln}_2\text{TiO}_5$ . The compounds were obtained by the simultaneous precipitation of the components from aqueous solutions and subsequent heating of the charge produced, which was then investigated by thermal and roentgenographic methods. Thermogravimetric analysis showed the presence of three endothermic effects on the thermal analyses of all specimens that corresponded to multistage elimination of decomposition products of the metal hydroxycarbonates. The x-ray studies showed that crystallization of rare earth-titanium-containing compounds occurs at 950-1,100°C while niobium-containing rare earth compounds are fully crystallized at 1,150°C. Bismuth-containing specimens crystallize at still lower temperatures. Isomorphically substituted  $\text{LaNdTiO}_5$ ,  $\text{LaYTiO}_5$ , and  $\text{NdYTiO}_5$  were obtained, all with a rhombic structure. Replacement of the rare earth elements with calcium and strontium can yield compounds with a fluorite structure. The compounds are basically equal in

their properties to known series-produced thermoresistive materials. They are suitable for use at high temperatures. Figures 3, references 8: 7 Russian, 1 Western.

UDC 546.65.535.373.4

**Luminescent Properties of Solid Solutions of  $\text{Y}_{1-x}\text{Ln}_x\text{BO}_3$  ( $\text{Ln} = \text{Pr}^{3+}, \text{Sm}^{3+}, \text{Dy}^{3+}, \text{Ho}^{3+}, \text{Er}^{3+}, \text{Tm}^{3+}$ )**

*18410111B Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 54 No 11, Nov 88 (manuscript received 2 Jun 87) pp 1130-1134*

[Article by V. P. Dotsenko, N. P. Yefryushina, V. A. Bolshukhin, T. Z. Seyfullina, and V. A. Chopovskiy, Institute of Physics and Chemistry, Ukrainian Academy of Sciences, Odessa]

[Abstract] A study is made of the spectral-luminescent properties as well as certain light-physical characteristics of solid solutions of  $\text{Y}_{1-x}\text{Ln}_x\text{BO}_3$ , where Ln is  $\text{Pr}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Ho}^{3+}$ ,  $\text{Er}^{3+}$ , or  $\text{Tm}^{3+}$ . Phase compositions were determined by x-ray diffraction diagrams. The solid solutions were produced by two-stage heat treatment of a charge containing coprecipitated rare-earth oxalates and boric acid. Usage tests of the luminescent materials based on yttrium orthoborate were performed under conditions eliminating temperature damping of the luminescence. It was found that electron bombardment resistance is little dependent on activator type and concentration. Concentration damping with the  $\text{Sm}^{3+}$  ion may be related to cross-relaxation transitions. Figures 3, references 12: 8 Russian, 4 Western.

UDC 541.117:541.15:541.64::547.391.1-38:541.49:546.7

**Production and Reactivity of Metal-Containing Monomers. Report 9. Low-Temperature Postradiation Polymerization of Metal-Containing Monomers Upon Devitrification of Matrices**  
*18410112f Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHMICHESKAYA in Russian No 11, Nov 88 (manuscript received 3 Jun 87) pp 2507-2511*

[Article by M R. Muydinov, G. I. Dzhardimaliyeva, B. S. Selenova, A. D. Pomogaylo, and I. M. Varkalov, Institute

of Chemical Physics, USSR Academy of Sciences, Chernogolovka]

[Abstract] A study is made of the possibility of low-temperature postradiation polymerization of typical metal-containing monomers—acrylates of Ni (II), Co (II), Cu (II), Cr (III) and Mn (II), acrylamide complexes of Co (II), Ni (II), and alcoxy derivatives of Ti (IV). Studies were performed in the low-temperature range, some in a 10 percent ethanol solution. The possibility is demonstrated of postradiation polymerization of the monomers upon devitrification in their own matrix and in the alcohol solutions. Postpolymerization of the monomers upon devitrification is more effective than is postpolymerization of their analogues, which do not contain metal atoms. Figures 3, references 10: 8 Russian, 2 Western.

UDC 541.138.2

**Trialkylphosphine Cation-Radical-Initiation of Free-Radical Addition of Dialkylthiophosphites to Alkenes**

18410095a Leningrad ZHURNAL OBŞHCHEY  
KHIMII in Russian Vol 59 No 1, Jan 89 (manuscript received 3 Nov 87) pp 223-224

[Article by A. S. Romakhin, V. A. Zagumennov, Ye. V. Nikitin and Yu. M. Kargin, Kazan State University imeni V. I. Ulyanov-Lenin]

[Abstract] It was shown that cation radicals of trialkylphosphines initiate addition of dialkylthiophosphites to alkenes: electrochemical oxidation of tripropyl- or triethylphosphine in presence of  $(RO)_2P(S)H$ , sodium perchlorate, olefine and trisodiumphosphate yielded  $O,O'$ -dialkylalkylthiophosphonate. The  $R_3P$  cation radicals initiated by an anode oxidation captured hydrogen atoms from  $(RO)_2P(S)H$  forming the protonated form  $R_3P^+H$  which under the influence of trisodiumphosphate converted to the starting phosphine, while the  $(RO)_2P(S)$  radical initiated the chain process of the addition of  $(RO)_2P(S)H$  to the double bond of an alkene. The following compounds were obtained in this fashion:  $O,O'$ -diethylcyclohexylthiophosphonate, B.P. 107-109°C (2 mm Hg),  $n_D^{20}$  1.4931;  $O,O'$ -dibutylcyclopentylthiophosphonate, B.P. 116-117°C (2 mm Hg),  $n_D^{19}$  1.4770 and  $O,O'$ -diisopropylhexylthiophosphonate, B.P. 93-94°C (1 mm Hg),  $n_D^{19}$  1.4541. References 2 (Russian).

UDC 547.1'118

**Synthesis of Toly-N,N-dibutylcarbamoylmethylphosphinic Acid**

18410095b Leningrad ZHURNAL OBŞHCHEY  
KHIMII in Russian Vol 59 No 1, Jan 59 (manuscript received 17 Nov 87) pp 225-226

[Article by V. A. Chauzov, Yu. N. Studnev, M. G. Iznoskova and A. V. Fokin]

[Abstract] It is shown that alkylation of 0-trimethylsilyl-0-isoamyl(tolylphosphonite) (I) with dibutyl amide of chloracetic acid yields tolyl-N,N-dibutylcarbamoylmethylphosphinic acid, M.P. 75-81°C, a compound difficult to synthesize by other methods. The starting material was obtained from a mixture of 0-isoamyl(tolylphosphonite), triethylamine and trimethylchlorasilane in benzene and used without isolation.

**Selective Synthesis of Thiaminediphosphate**

18410095c Leningrad ZHURNAL OBŞHCHEY  
KHIMII in Russian Vol 59 No 1, Jan 89 (manuscript received 27 Nov 87) pp 226-227

[Article by S. V. Zabrodskaya, D. A. Oparin and Yu. M. Ostrovskiy, Institute of Biochemistry, BSSR Academy of Sciences, Grodno]

[Abstract] In the past, it has been difficult to obtain selectively phosphorylated thiamine, the usual reaction products consisting of a mixture of difficult to separate phosphates. It

is shown here that a 1 to 3 hr phosphorylation of thiamine with a 2:1 mixture of orthophosphoric acid:phosphorus oxide at 8-10 mm Hg pressure and 100-120°C produces a high yield (70-80%) of thiaminediphosphate exclusively. Extension of the reaction time or an increase in temperature leads to formation of thiamine monophosphate. References 2: 1 Russian, 1 Western.

UDC 543.422:541.6:547.1'118

**Dicomponent Equilibrium of 2-Phenyl-2-thio-5,6-benzo-1,3,2-dioxaphosphepine Chair Forms Based on Combination Light Scattering Spectra**

18410095d Leningrad ZHURNAL OBŞHCHEY  
KHIMII in Russian Vol 59 No 1, Jan 89 (manuscript received 12 Feb 88) pp 228-229

[Article by I. Kh. Shakirov, R. R. Shagidullin, R. P. Arshinova and R. A. Kadyrov, Institute of Organic and Physical Chemistry, Kazan Branch, USSR Academy of Sciences; Chemical Institute imeni A. M. Butlerov, Kazan State University imeni V. I. Ulyanov-Lenin]

[Abstract] Earlier spectroscopic studies of 5,6-benzo-1,3,2-dioxaphosphepines with NR<sub>2</sub>, OPh or OMe groups at the phosphorus atom showed that they exist in chair and twist (or twist-boat) conformations. Characteristic bands were identified for both of these forms. In the present study, absence of the twist form was noted in 2-phenyl-2-thio-5,6-benzo-1,3,2-dioxaphosphepine. Analysis of combination light scattering and IR spectral data indicated presence of two chair forms: in the liquid state and chair with an axial Ph group predominated (it was more polar and energetically less advantageous) while in the crystalline phase the chair form existed with an equatorial Ph-group and an axial P=S. References 6: 5 Russian, 1 Western.

UDC 547.341

**Phosphorus Containing Chlorotethenylchloroformamidines Obtained From N-Acetylurea**

18410095e Leningrad ZHURNAL OBŞHCHEY  
KHIMII in Russian Vol 59 No 1, Jan 89 (manuscript received 24 Nov 87) pp 227-228

[Article by M. Yu. Dmitrichenko, V. I. Donskikh, V. G. Rozinov, G. V. Dolgushin, G. V. Ratovskiy, V. G. Yefremov and V. V. Rybkina, Irkutsk State University]

[Abstract] It had been reported earlier that reaction of phosphorus pentachloride with N-acetylurea in a 3:1 ratio gave 2,4,4,6-tetrachloro-1,3,4-diazaphosphorene. When the ratio of reaction components was increased to 5:1, the product was a complex compound 4-(trichlorophosphazo)-2,4-dichloro-3-aza-1,3-butadienyltrichlorophosphonium hexachlorophosphorate (I). Upon reaction with formic acid, I gave N<sup>1</sup>-dichlorophosphoryl-N<sup>2</sup>-(1-chloro-2-dichlorophosphoryl-ethenyl)-0-chloroformamidine, M.P. 108-111°C. NMR and IR spectra of both products are reported. References 3: 2 Russian, 1 Western.

UDC 543.426:541.49:547.963.3:547.857.7

**Complex Formation of Certain Pesticides With Adenosine Triphosphoric Acid**

*18410112e Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHMICHESKAYA in Russian No 11 Nov 88 (manuscript received 19 Jun 87) pp 2501-2507*

[Article by Ye. A. Saratovskikh, T. A. Kondrateva, B. L. Psikha, R. I. Gvozdev, and V. G. Kartsev, Institute of Chemical Physics, USSR Academy of Sciences, Chernogolovka]

[Abstract] Results are presented from studies of the interaction of pesticides with ATP, using eight common pesticides (six herbicides and two fungicides) and

synthetic metal complexes of one of them—the herbicide Lontrel. Fluorescence spectra were recorded in a quartz cuvette by using a 312-nm excitation wave, with maximum fluorescence emission at 420 nm for ε-ATP and 290 and 380 nm for ATP. It was found that the pesticides (Bazagran, Zenkor, Kuzagard, Lontrel, Roundup, Sepoxidim, Tachigaren, and Tilt) and metal complexes of Lontrel form complexes with nucleotides in a 1:1 composition. The values of the complexing constants were determined. The strength of nucleotide complexes with metal-Lontrel complexes was found to depend on the nature of the metal ion. Copper, cobalt, and nickel complexes of Lontrel with nucleotide are significantly stronger than is the Lontrel-nucleotide complex. References 14: 9 Russian, 5 Western.

UDC 553.983.002.61:543.82

**Effect of Pyrite on Yield and Composition of Oil Shale Semicoking Products. 2 Communication. Shale Oil Kukersite**

*18410153a Tallinn IZVESTIYA AKADEMII NAUK ESTONSKOY SSR: KHIMIYA in Russian Vol 38 No 1, Jan-Mar 89 (manuscript received 12 Apr 88) pp 6-10*

[Article by V. Vysotskaya and K. Urov, Institute of Chemistry EstSSR Academy of Sciences]

[Abstract] Mixtures of flotation concentrates of Kukersite kerogen and pyrite were described in previous paper along with the methodology. Analysis of the present data showed that analogously to thermal decomposition of dictyonema shale, the behavior of pyrite in respect to thermal destruction of kerogens was very similar: increased content of pyrite in the starting material used in semicoking led to a decreased yield of tar; kerogen hydrogen and pyrite sulfur combined to yield H<sub>2</sub>S quantities in excess of the calculated levels based on the starting shale oil. It was presumed that the catalytic effect of pyrite was due just to the H<sub>2</sub>S forming in the process. Because pyrite underwent chemical conversion during this process, it could not be considered to have acted as a true catalyst. Figures 3; reference: 1 (Russian).

UDC 665.612.3[571.16]

**Tomsk Oblast Gas Condensates**

*18410091 Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 11, Nov 88 pp 8-11*

[Article by G. B. Nemirovskaya, L. S. Blinova, T. V. Sechina, and S. I. Smolyaninov, Tomsk Polytechnical Institute imeni S. M. Kirov]

[Abstract] Data are presented on the composition and properties of condensates from Rechnyy, Kalinovoy, and Gerasimovskiy deposits in the Tomsk Oblast. Curves illustrate the group hydrocarbon and fractional composition of the condensates. The gasoline fractions of the Kalinovoy and Gerasimovskiy condensates have a low content of aromatic hydrocarbons and a high content of methane hydrocarbons, particularly iso-M. The maximum content of naphthenic hydrocarbons is in the 95-122°C fraction. Rechnyy condensate is distinguished by its high content of aromatics (up to 29 percent) and naphthenics (up to 38-57 percent). The medium and high-boiling fractions of these gas condensates can be recommended as components for various reagents and diesel fuels. The yield of diesel distillates at 180-350 and 180-300°C is 12.5-22.8 percent. This fraction meets the norms for summer diesel fuel except for its high acidity.

The diesel distillates of Kalinovoy and Gerasimovskiy condensates are suitable as winter diesel fuel for temperate zones. Figure 1; references 9: Russian.

UDC 665.642.3.092.147.3

**Influence of Moving Liquid-Metal Film on Pyrolysis of Gasoline Fractions**

*18410091b Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 11, Nov 88 pp 14-17*

[Article by G. V. Mamantov, I. V. Beletskiy, V. A. Pozdnyakov, A. D. Reznikov, and Yu. M. Zhorov, All-Union Scientific Research Institute of Petroleum Machinery, Moscow Institute of Oil and Gas imeni I. M. Gubkin]

[Abstract] A study is made of the influence of the flow of a film of molten metal on the yield of end products and intensification of pyrolysis of the gasoline fraction. Studies were performed on an installation that allows pyrolysis both with and without the flow of molten metal film. Pyrolysis gases were chromatographically analyzed with a heat conductivity detector. The quantity of coke formed during the experiment was measured. The melt used was a eutectic alloy of lead and bismuth, 44.5:55.5 mass parts, and a melting point of 125°C. Studies were performed at 700-830°C with a contact time of 0.2-1.2 s and a water vapor of 0 to 50 percent by mass of the raw material. The experiment data indicated that gas formation increases with increasing temperature and that the yield of propylene and butenes passes through a gentle maximum. A continuously recirculated liquid metal film can fully eliminate coking of the heat-transfer surface of the equipment, thus decreasing or completely eliminating dilution of the raw material with water vapor, which in turn increases the productivity of the reaction volume with respect to the raw material charged. Figures 3, references 6: 5 Russian, 1 Western.

UDC 665.652.4.095.253.73:546.226-325

**Influence of Catalytic Complex Composition on Octane Number of Alkyl Gasoline**

*18410091c Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 11, Nov 88 pp 17-18*

[Article by I. T. Tagarov, V. T. Sumanov, and S. N. Khadzhiyev, Groznensk Institute of Petroleum]

[Abstract] The interrelationship of the quality of alkyl gasoline and composition of its catalytic complex was studied directly on an industrial installation for sulfuric acid alkylation by utilizing a complex catalyst consisting of sulfuric acid, organic compounds, and water. The results of the study indicate the complex influence of the composition of the catalytic system on the octane number of the gasoline produced (end boiling temperature, 205°C). The maximum octane number is observed at 94-95 percent acid by mass, but there is a significant dispersion of results. Other components of the catalytic

system—the organic compounds and water—also influence the octane number of the product. The concentrated acid poorly catalyzes the alkylation reaction, thus forming heavy, low-octane products. Up to a certain point, increasing the content of organic impurities improves dissolution in the isobutane complex, which in turn improves the conditions of formation of trimethylpentanes and the quality of the gasoline. A small quantity of water, about 2 percent by mass, also helps to accelerate transfer of the hydride ion and improve the quality of the gasoline. The best octane number (97) is achieved by a catalytic system containing 3.5 percent organic compounds by mass, less than 2 percent water, and 94.5-95 percent sulfuric acid. Figures 2, references 7: 5 Russian, 2 Western.

UDC 665.765:621.892

**Estimating Movement of Plastic Lubricants in Friction Couples by Means of Finely Dispersed Metal-Containing Compounds**

18410091 Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 11, Nov 88 pp 21-22

[Article by Yu. I. Barash, V. V. Sinitsyn, deceased, G. M. Balak, and I. G. Fuks, All-Union Scientific Research Institute of Railroad Transport, Moscow Institute of Oil and Gas imeni I. M. Gubkin]

[Abstract] The authors have developed a technically simple method to label plastic lubricants. The method allows very accurate determination of the content of the label substance in the lubricant. The label consists of finely dispersed aluminum and molybdenum disulfide powder with particle sizes of not over 25 and 7  $\mu\text{m}$ . The use of this label is limited by the cation composition of the basic lubricant. For lubricants based on soap thickeners other than aluminum, the label can be compounds of aluminum and other metals (other than molybdenum). The label was mechanically dispersed in sodium-calcium lubricant, and the contents were determined by atomic absorption spectrophotometry. A charge of lubricant was heated to 920K for 2 hours. The ash was acid treated in 20 percent hydrochloric and concentrated sulfuric and concentrated nitric acids. Next, the mixture was heated to decoloration and disappearance of the sediment, diluted with 7-10 times excess water, and analyzed by atomic absorption spectrophotometry. Analysis of 20 specimens does not require more than 4 hours. The method allows a very accurate quantitative determination of the degree of mixing of lubricants from various zones in a bearing unit. Several labels can be used simultaneously to study processes of the mixing of lubricants in units. References 4: 3 Russian, 1 Western.

UDC 621.892.097

**Biological Damage to Lubricant Materials**

18410091e Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 11, Nov 88 pp 22-24

[Article by Ye. G. Toropova, A. A. Gerasimenko, A. A. Gureyev, I. A. Timokhin, G. V. Matyusha, and A. A. Belousova, Moscow State University imeni M. V. Lomonosov; Moscow Institute of Oil and Gas imeni I. M. Gubkin]

[Abstract] A study is made to determine the biological damaging factor in lubricant materials when they have been stored for a long period of time and when various products are used. Samples were taken from items of equipment in long-term use under various climatic conditions. The specimens were evaluated from the standpoint of their external appearance, examined under a microscope, placed in nutrient media, and cultured. The bioresistance of fresh oils for the cultures produced was studied, and their corrosive microorganisms were identified. Corrosive microorganisms were found in 80 percent of the lubricant material samples taken. Oils are contaminated with biological agents during the storage and use of equipment under both cold and hot climate conditions. Some 37 cultures were identified in all. The results indicate the need to consider the biological contamination factor of oil in the long-term use and storage of equipment. Tributyl tin oxide and alkyl phenoxytriethyl stannane, oil-soluble liquids at room temperature, were the most effective biocides found for the cultures of microorganisms isolated from the oils. References 4: Russian.

UDC 543.544[0.88.8]

**Express Method of Determining Lead Content in Gasolines**

18410091f Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 11, Nov 88 pp 39-40

[Article by A. I. Lavrinenko, Technical Thermal Physics Institute, Ukrainian Academy of Sciences]

[Abstract] Flame atomic absorption analysis is more effective than is the standard method of spectrophotometric determination of lead in gasoline. The specimen to be studied is atomized in a propane-air or other special flame and exposed to radiation with a discrete spectrum that is characteristic for the impurity being analyzed, and the absorption of the resonant frequency is measured (for lead, a wavelength of 283.3 nm). The measured signal is proportional to the concentration of the impurity. Test methods based on this technique are used by foreign firms. Chemical treatment of the specimens before analysis is not required, which reduces analysis time to 20-30 seconds. The method allows express analysis of ethylated gasoline with a broad range of lead concentrations. Figure 1, references 6: Russian.

UDC 629.063.001.4

**Fuel Transport System for Liquefied Natural Gas**

18410117c Moscow KHIMICHESKOYE I NEFTYANOYE MASHINOSTROYENIYE in Russian No 1, Jan 89 pp 13-15

[Article by V. V. Veselov, engineer, A. M. Domashenko, candidate of technical sciences, and N. V. Filin, doctor of technical sciences]

[Abstract] Problems related to the use of liquefied natural gas as a motor fuel are discussed. A cryogenic fuel tank design that uses a powder-vacuum insulation system is proposed. Experiments were performed involving

zero-drainage storage of liquid nitrogen with oscillations having a frequency of 1.6 Hz and an amplitude of 20 mm to simulate use of the tank in a moving vehicle. If gases are allowed to vent from the tank, significant loss of fuel drops is observed when the tank is vibrating. The installation of special settling devices on the pipelines is found to reduce drop transfer of the product and the entry of liquid product into the pipelines by a factor of 8-10. Figures 3, references 7: Russian.

UDC 658.511.5:66.023

### Promising Radial Reactor Designs

18410117a Moscow *KHIMICHESKOYE I NEFTYANOYE MASHINOSTROYENIYE* in Russian  
No 1, Jan 89 pp 8

[Article by V. S. Genkin, A. V. Gribanov, and G. V. Mamontov, candidates of technical sciences]

[Abstract] A quantitative estimate is given of the separation effect of the precipitation of particles into the circular gap of a radial reactor. The critical particle movement speed at which particles are carried into the catalyst layer by the flow through the perforated surface is equal to the radial flow speed. Computations for a typical reforming reactor showed the critical diameter to be 80-160 mm. Particles of this size represent about 10 percent of the total number of particles in the flow. This can cause up to 10 percent of the catalyst volume to be blocked. Future radial reactor designs must allow for the collection of separated mechanical particles in the bottom portion of the equipment, which in present designs is filled with porcelain balls supporting the catalyst layer. This design, together with the effect of the separation purification of the gas flow, makes it possible to increase the device's reaction space and thus decrease its metal consumption and improve its reliability.

UDC 621.59:621.521.004.14

### Providing Vacuum in Heat-Insulating Cavities of Cryogenic Equipment

18410117b Moscow *KHIMICHESKOYE I NEFTYANOYE MASHINOSTROYENIYE* in Russian  
No 1, Jan 89 pp 9-13

[Article by V. Ye. Kurtashin, engineer, V. I. Kupriyanov, candidate of technical sciences, and V. M. Yermokhin, engineer]

[Abstract] Problems related to supporting the vacuum in the insulating spaces of cryogenic equipment are discussed. The transition to modern vacuum absorbents is now nearly complete. These absorbents include specialized zeolite, activated carbon, and carbon fabric, which may be applied directly to the walls of vacuum spaces to ensure that the material is rapidly cooled and begins adsorbing residual gases in the vacuum space. A new hydrogen absorbing material has now been developed, palliated manganese dioxide (PMD), which has four

to five times greater sorption capacity than silver oxide does, which was previously used for the same purpose. Equations are produced that describe the liberation of gases by structural materials at very low pressures. Studies were performed on the variation in regeneration coefficient and diffusion of moisture in zeolites and active carbon adsorbents as functions of the residual moisture content. The studies can be used for the proper selection of operating materials and conditions. Figures 6, references 7: Russian.

UDC 621.51.001.4:620.1.05

### Developmental Test System of Gas Pumping Installations With Aviation Drive

18410117d Moscow *KHIMICHESKOYE I NEFTYANOYE MASHINOSTROYENIYE* in Russian  
No 1, Jan 89 pp 23-24

[Article by N. G. Krivshich, candidate of technical sciences, V. M. Minko and A. P. Usatenko, engineers, and A. M. Khoroshchenko, candidate of technical sciences]

[Abstract] This article describes the process of the developmental testing of a new gas-pumping installation used at the All-Union Scientific Research Institute of Compressor Building, the testing of models of newly developed units and systems to evaluate the correctness of selection of basic parameters and characteristics, and start-to-finish state acceptance testing of the system (which is intended to ensure that the installation conforms to the technical specifications, requirements, standards, and technical documentation). The process continues with periodic testing to evaluate the stability of equipment characteristics in series production, which is followed by improvements and modifications in the design and manufacturing process of equipment in series production. A flowchart of the developmental testing process is presented.

UDC 547.759.32:665.61.033.53

### Alkylcarbazoles of Samotlorskaya Petroleum

18410124a Moscow *NEFTEKHIMIYA* in Russian  
Vol 28 No 5 Sep-Oct 88 (manuscript received  
10 May 88) pp 596-601

[Article by Ye. B. Grolov and N. A. Vanyukova, Institute of Petrochemical Synthesis imeni A. V. Topchiyev, USSR Academy of Sciences, Moscow]

[Abstract] Data are presented on the individual compositions of alkylcarbazoles separated by a chromatographic method of exhaustive and selective extraction from Samotlorsk deposit petroleum. Gas-liquid chromatographic analysis was performed in quartz, copper, and steel capillary columns with OV-101, apiezon-L, and dexyl-400 stationary phases in a stream of hydrogen gas. Nineteen derivatives of carbazole are detected, including several found for the first time in petroleum: 1,8-di,

1,3,8-, 1,4,8-, 1,3,5-, 2,4,8-tri-, and 1,3,5,8-tetramethylcarbazoles and 1-ethyl-, 1-, and 4-n-propylcarbazoles. Tri- and tetramethyl carbazoles predominate among alkyl carbazoles, with substituents at positions 1 or 1.8. These isomers have better solubility in saturated hydrocarbons. Figure 1, references 14: 5 Russian, 9 Western.

UDC 547.677.2:665.61.033.25

### Segregation of Phenanthrene Hydrocarbons From High-Boiling Point Petroleum Fractions

18410124b Moscow NEFTEKHIMIYA in Russian  
Vol 28 No 5, Sep-Oct 88 (manuscript received  
4 Jan 88) pp 602-605

[Article by E. G. Lekveyshvili, L. D. Melikadze, A. A. Polyakova, M. N. Tevdorashvili, L. O. Kogan, R. N. Semanyuk, and M. I. Tokarev, Institute of Physical and Organic Chemistry imeni P. G. Melikishvili, Georgian Academy of Sciences; All-Union Scientific Research Institute of Oil Refining]

[Abstract] A study is made of the composition and structure of aromatic hydrocarbons segregated from petroleum by the reaction of photocondensation with maleic anhydride. The studies were performed on products of the chromatographic separation of aromatic Norilsk petroleum fraction concentrate, boiling in the 500-510°C interval, and on the 460-475°C fraction of Mirzaani petroleum. The method of separating phenanthrene hydrocarbons and their benzo derivatives from petroleum by the reaction of photocondensation with maleic anhydride is found to yield concentrates with up to 80 percent content of these hydrocarbons. The results demonstrate the effectiveness of the method for the segregation and separation of phenanthrene hydrocarbons both for high-boiling-point aromatic fractions and for broader fractions. The content of phenanthrene hydrocarbons in the aromatic concentrate is 69.9 percent for the Norilsk petroleum and 62.0 percent for the Mirzaani petroleum, and the respective degrees of extraction of aromatic hydrocarbons are 57.7 and 52.2 percent. References 9: Russian.

UDC 547.592.1:542.941.8:665.644.4

### Kinetics of Dehydrogenation of Cyclohexane on Coked Polymetallic Reforming Catalyst

18410124c Moscow NEFTEKHIMIYA in Russian  
Vol 28 No 5 Sep-Oct 88 (manuscript received  
3 Sep 87) pp 618-622

[Article by Yu. A. Skipin, A. V. Grishchenko, A. A. Polyakov, V. V. Chulkova, and V. S. Fedorov, Lenneftekhim Scientific-Production Association]

[Abstract] Specimens of polymetallic KR-104A catalyst, coked in the reactor of an industrial installation, were studied to determine the mechanism of deactivation of

reforming catalysts by coke. The installation was operated without any deviation from the normal technological conditions and produced 92-octane reformate from the 85-180°C fraction of straight-run gasoline. The catalyst was 0.36 percent platinum, 0.20 percent rhenium, and 0.25 percent cadmium on  $\gamma\text{-Al}_2\text{O}_3$ . It was removed after 1 year of operation from the middle of the head reforming reactor. For fresh catalyst, the activation energy of the reaction was higher than for the coked specimens due to their higher content of cadmium, which is removed from the catalyst as it is used. With increasing coke content, the benzene adsorption factor and activation energy of the reaction increased slightly. Figures 3, references 5: 2 Russian, 3 Western.

UDC 547.535.2:66.094.187:541.127

### Kinetics and Mechanism of Dehydrogenation of Ethyltoluenes on Oxide Vanadium-Containing Catalysts

18410124d Moscow NEFTEKHIMIYA in Russian  
Vol 28 No 5 Sep-Oct 88 (manuscript received  
16 Jun 87) pp 623-627

[Article by O. V. Zolotarev, I. Ya. Petrov, and B. G. Tryasunov, Kusnets Basin Polytechnical Institute, Kemerov]

[Abstract] A study is made of the kinetics of the dehydrogenation of ethyltoluenes to vinyltoluenes on a  $\text{V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$  catalyst with added nickel and sodium oxides. Experiments were performed on a recirculating installation at atmospheric pressure with direct input of hydrocarbon vapors and water. A narrow fraction of m- + p-ethyltoluenes was used that was isolated from aromatic C<sub>9</sub> gasoline reforming fractions containing 7 percent mesitylene and 3 percent pseudocumene. It is shown that the main and secondary reactions of the dehydrogenation process occur in parallel and form vinyltoluenes in the main process and benzene, toluene, xylenes, ethylbenzene, and styrene in the secondary process. The reaction rate equations are similar to rational fraction equations. Figure 1, references 10: 6 Russian, 4 Western.

UDC 547.215:665.64.097.3:661.183.6

### Mechanism of Decomposition of Isopentane on Very High Silica Zeolites

18410124e Moscow NEFTEKHIMIYA in Russian  
Vol 28 No 5, Sep-Oct 88 (manuscript received  
13 Sep 87) pp 662-666

[Article by T. M. Gayrbekov, R. A.-V. Turluyev, A. K. Manovyan, and S. N. Khadzhiiyev]

[Abstract] Cracking of isopentane on very high silicon zeolites subjected to various types of processing is studied in order to determine a possible conversion mechanism. Studies were performed on very high silica zeolite specimens with a particle size of 0.08 mm in decationized form and Si/Al ratios of 20, 65, 83, and 104. The experiments were performed in a microcatalytic installation in the kinetic area. Conversion was restricted to less than 10 percent so as to decrease the influence of secondary reactions. A superacid mechanism is suggested for cracking of isopentane on

the zeolites, including protolysis of the C-C and C-H bonds and alkylolysis of C-C bonds of the isopentane molecule. Varying the Si/Al ratio of the zeolites, heat, and steam treatment, increasing the preliminary heat treatment and the degree of coking of the catalyst can apparently increase the selectivity of the reaction of protolysis of the C-H bond and decrease the selectivity of the C-C bond protolysis reaction. Figure 1, references 15: 8 Russian, 7 Western.

UDC 665.73:66.092.41:661.183.6

**Conversion of Pyrolytic Gasoline With Zeolite-Containing Catalysts Present**  
*18410124f Moscow NEFTEKHIMIYA in Russian Vol 28 No 5, Sep-Oct 88 (manuscript received 11 Mar 88) pp 667-669*

[Article by L. Novakovski and T. Sudol, Higher Engineering School, Pedagogic Institute, Opole, Poland]

[Abstract] Results are presented from a study of the transformation of pyrolytic gasoline in the presence of zeolite-containing CaHY, CeHY, and MZ-5 catalysts. Experiments were performed in a continuous tubular reactor of heat-resistant glass with a stationary catalyst at 789-863 K and a contact time of 0.21-0.60 s. It was found that the quantity of ethylene in the gaseous reaction products did not change and did not exceed 7.5 mass percent in the time and temperature intervals studied. The maximum level of total lower olifens was 47.7 percent, and the maximum quantity of propylene was 38.4 percent. They were obtained in the presence of the industrial catalyst MZ-5. References 8: 5 Russian, 3 Western.

UDC 678.664.01

**Reinforcement of Thermoplastic Polyurethane Semicarbazides by Synthetic Fibers**

18410085a Kiev KHIMICHESKAYA

TEKHNOLOGIYA:

NAUCHNO-PROIZVODSTVENNYY SBORNIK in Russian No 6 Nov-Dec 88 (manuscript received 28 Jul 87) pp 13-17

[Article by L. B. Goncharova, A. P. Grekov, N. A. Kuzmak, and L. A. Kosenko, Institute of High-Molecular Mass Compound Chemistry, Ukrainian Academy of Sciences, Kiev]

[Abstract] This study examines the specifics of the reinforcement of thermoplastic polyurethane semicarbazides by synthetic fibers and the physicomechanical and thermal properties of film materials based on them. The initial polymer used was polyurethane semicarbazide synthesized from oligooxytetramethylene glycol, 4,4'-diphenylmethane diisocyanate, and isophthalic acid dihydrazide. The fillers used were nylon and spandex fibers, which were first heated in a vacuum for several hours. The polymers were filled with dispersed finely chopped polymer fibers in 25 percent dimethylformamide. The composites were then vacuum treated, poured onto glass, and dried 6 hours at room temperature and 3-4 hours at 50-60°C. The composites contained 1-5 percent nylon fiber, 5-90 percent spandex. Spandex-reinforced composite acted as polymer mixtures with both phases continuous so that it was impossible to speak of one phase as dispersed within the other. The phase interface is quite unstable, and one polymer is emulsified within the other, causing a drop in heat capacity at the glass-transition point in a 50 percent spandex composite. The nylon fiber mainly influences the glass-transition point of rigid segmented domains; this also increases the system's elasticity. Figures 2, references 11: 10 Russian, 1 Western.

UDC 661.183.2:66.095.5

**Activation of Styrene-Divinylbenzene Copolymer in Fluidized Bed**

18410085d Kiev KHIMICHESKAYA

TEKHNOLOGIYA:

NAUCHNO-PROIZVODSTVENNYY SBORNIK in Russian No 6, Nov-Dec 88 (manuscript received 11 Jul 88) pp 45-51

[Article by V. V. Artyushenko, V. N. Aleksandrov, A. P. Kozhan, and V. S. Ryabchuk, Petrochemistry Department, Institute of Physical and Organic Chemistry and Coal Chemistry, Ukrainian Academy of Sciences, Kiev]

[Abstract] This article examines the effect of the technological parameters of the process of the activation of sulfated styrene-divinylbenzene copolymer in a fluidized bed on the physical and chemical characteristics of the adsorbents produced. It is found that by changing the

process parameters, high-strength spherical sorbents can be created on the basis of industrial type KU 23-4D/100 carbonizate. The sorbents created have well-developed pore surfaces. Carbon adsorbents produced from styrene-divinylbenzene copolymer were tested by the Institute of Problems of Oncology, Ukrainian Academy of Sciences. They were found to have high sorption activity for a number of toxins, which makes them suitable for use in clinical practice. Figure 1, references 16: 15 Russian, 1 Western.

UDC 541.64:547.495.1:546.26.162

**Electroinitiated Polymerization of Aliphatic Isocyanate-Containing Oligomer With Carbon Fibers Present**

18410111e Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 54 No 11, Nov 88 (manuscript received 16 Jul 87) pp 1213-1216

[Article by V. G. Matyushova, T. E. Lipatova, and K. V. Mudrak, Institute of High-Molecular Mass Compounds, Ukrainian Academy of Sciences, Kiev]

[Abstract] A study was made of the anion polymerization of an unsaturated isocyanate-containing oligomer obtained by reacting ethylene glycol monomethacrylic ester and hexamethylene diisocyanate. The compound investigated was examined as a model of a composite material of a mixture of oligomers containing three isocyanate groups and unsaturated bonds. During the process of polymerization, a polymer is formed on the surface of the carbon fiber, which increases the mass of the fiber after electrolysis by 500 percent. The polymer liberated onto the surface of the fiber is poorly soluble in organic solvents, and after extraction about 450 percent polymer remains on the fiber. The polymer is nonuniformly distributed over the surface of the fiber, probably as a result of defects in the carbon fiber structure. Figures 2, references 7: 5 Russian, 2 Western.

UDC 678.742.2-9.546

**Flammability of Certain Chlorine-Containing and Carbon Chain Elastomers**

18410119a Moscow KAUCHUK I REZINA in Russian No 1, Jan 89 pp 11-12

[Article by G. M. Ronkin, B. B. Serkov, and A. S. Izmaylov]

[Abstract] The flammability of raw and chlorinated elastomers was estimated on the basis of the oxygen index. The analysis showed that the introduction of chlorine to the molecular chain of the polymers decreases their flammability. Chlorinated polyethylene containing over 54 percent chlorine and flame-resistant fluorine rubbers have approximately the same oxygen index. Production batches of the product have a somewhat lower oxygen index than do unstabilized materials,

probably due to a difficulty in dehydrochlorination of the stabilized polymers. The value of the oxygen index increases with increasing chlorine content. References 5: 4 Russian, 1 Western.

UDC 678.701:54-185:541.24

**Molecular Parameters of Mixtures Prepared From Raw Rubbers With Different Molecular Masses**  
*18410119b Moscow KAUCHUK I REZINA in Russian No 1, Jan 89 pp 12-13*

[Article by N. I. Urazov, L. V. Kovtunenko, and A. P. Garshin]

[Abstract] A study was made of the molecular parameters of mixtures prepared of DSSK-18 raw rubbers of different molecular masses. Equations are presented for computation of the molecular masses of the products based on the quantities and molecular masses of the substances mixed. Satisfactory agreement is achieved between the calculated and experimental data. The possibility of using the equations obtained to predict the technological properties of mixtures and the physicomechanical characteristics of vulcanisates is demonstrated. References 8: 6 Russian, 2 Western.

UDC 678.046.2+661.666.4.011.002.612

**Properties of Tire Rubbers Filled With Modified Technical Carbon**

*18410119c Moscow KAUCHUK I REZINA in Russian No 1, Jan 89 pp 13-16*

[Article by S. A. Demidova, I. A. Ilin, V. M. Goncharov, and N. D. Zakharov, deceased]

[Abstract] Technical carbon was modified by adsorption of oligomers on its surface with selected reactive functional groups. The technical carbon thus acted as a carrier for the modifying additive, catalytically influencing its interaction with the other rubber mixture ingredients. The study confirmed the effectiveness, in tire rubber mixtures, of the use of type P514 technical carbon modified with nitrogen-containing oligomer compounds, including products of the reaction of the nitrogen-containing adamantane derivative with polymers consisting of aromatic rings connected by propane groups and containing various functional groups. It was found that the relationship of components in the modifiers essentially influences the properties of the rubbers. Optimal characteristics were found in rubbers containing modified technical carbon with ratio of initial components to modifier of 1:1. Also studied was the possibility of decreasing the content of industrial modifier and eliminating nonproductive carbon filler. It was found that the use of the modified carbon in tire rubber

improved adhesion, thereby allowing elimination of the filler and a reduced dose or elimination of type RU modifier. Figures 3, references 7: Russian.

UDC 541(64+14):539.3:547.452.81

**Mechanical Properties of Cotton Fiber Bombardeed With UV Rays During Maturation**

*18410122a Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 30 No 12, Dec 88 (manuscript received 26 Jun 87) pp 2509-2511*

[Article by M. Shermatov, Leninabad State Pedagogic Institute imeni S. M. Kirov]

[Abstract] The influence of UV radiation on the mechanical properties and structure of cotton fiber was studied when the cotton plants were irradiated during various stages of maturation by UV radiation at  $\lambda=253.7$  nm. Experiments were performed by using a tractor to carry a UV irradiator with a 1-kW generator, a 220-V voltage stabilizer, and a type OBN-150 UV lamp. The durability of the irradiated fibers was found to be higher than that of nonirradiated fibers. The strengthening effect of UV radiation appears when it is applied to the plants during the process of maturation of the fibers. UV irradiation of fibers already formed causes a decrease in strength and durability. Figures 4, references 6: Russian.

UDC 541.64:536.4:542.943

**Beginning and Ending Temperatures of Polymer Thermal Destruction Based on Structural Data**

*18410122B Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 30 No 12 Dec 88 (Manuscript received 29 Jun 87) pp 2523-2531*

[Article by A. A. Miroshnichenko, M. S. Platitsa, and T. P. Nikolayeva, All-Union Scientific Research Institute of Reagents and Chemically Pure Materials for Electron Technology]

[Abstract] A method is developed for determining the starting and ending temperatures of the thermal destruction of polymers based on group structural components. Analysis of the pyrolysis of polymers distinguishes a number of basic features in the chain of pyrolytic reactions, including breaking of the chain at the weakest bond, generation of two end radical groups and valence-saturated groups, transmission of a radical to another chain with splitting of a chain fragment (perhaps a monomer), evaporation of destruction products from the melt in molecular form, and splitting of chain fragments

or their reaction products. The algorithm is used to analyze the most probable mechanisms of the decomposition of polymer molecules. Figures 2, references 15: 14 Russian, 1 Western.

UDC 541.64:532.13:535,577

**Temperature Variation of Characteristic Viscosity and Birefringence of Certain Comb-Like Polymers With Mesogenic Side Groups**

18410122c Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 30 No 12, Dec 88 (manuscript received 29 Jun 87) pp 2532-2535

[Article by I. N. Shtennikova, Ye. V. Korneyeva, and G. F. Kolbina, Institute of High-Molecular Mass Compounds, USSR Academy of Sciences]

[Abstract] In order to study the influence of temperature on the conformational properties of comb-like macromolecules, measurements were taken of the variation in characteristic viscosity and birefringence in a stream as

functions of temperature for two thermotropic comb-like polymers: poly-p-n-methacryloyl oxyphenyl-lauryl-oxybenzoate and poly-p-methacryloyl benzoate-n-hexadecyl benzoate-hydroquinone. In all solvents in which the dimensions of the macromolecule and viscosity are low, increasing temperature causes an increase in viscosity and macromolecule size. In solvents in which the intramolecular reaction is determined by the large dimensions of the molecules, increasing the temperature decreases viscosity. The change in the macromolecular dimensions of the polymers studied as the temperature changes is also reflected in their optical characteristics. In those solvents in which viscosity increases with temperature, birefringence is proportional to the optical anisotropy of the macromolecules and decreases with increasing temperature. This change in birefringence reflects a change in the reactions of the side groups. Improving solvent quality decreases the convolution of the macromolecules and decreases the interaction of mesogenic groups, which decreases the intramolecular orientation of the side chains and thus decreases birefringence. Figures 4, references 9: 8 Russian, 1 Western.

UDC 546.799.3/4

**Extraction of Neptunium and Plutonium With Bi- and Polydentate Organophosphorus Compounds**  
*18410096a Leningrad RADIOKHIMIYA in Russian  
Vol 30 No 5, Sep-Oct 88 (manuscript received  
25 Nov 87) pp 614-618*

[Article by A. M. Rozen, Z. I. Nikolotova and N. A. Kartasheva]

[Abstract] Bidentate organophosphorus compounds are highly effective in extracting actinoids; extraction of Np(IV) and Pu(IV) with a number of bidentate and tridentate reagents (diphosphoric dioxides and carbamoylphosphoryl compounds) was studied. In previous work it was noted that while extracting americium(III) and various lanthanoids(III) with diphosphine dioxides, substitution of alkyl radicals by more electronegative phenyl groups led to increased coefficients of distribution and extraction. This phenomenon was called anomalous aryl intensification (AAI) of complexes. In the case of Np(IV) and Pu(IV), transition from tetraalkylmethylenediphosphine dioxide to the tetraaryl homologue resulted in an "apparent" AAI: the distribution coefficients increased while the extraction coefficients decreased. A different situation was observed with tridentate extractants: replacement of an alkyl substituent by a phenyl led to real AAI in which both the distribution and extraction constants were intensified. In the series carbamoylphosphonate-phosphinate-phospine oxide, the sum of the electronegativity of phosphane substituents decreases and the extraction and distribution coefficients for Np(IV) and Pu(IV) increase. Figures 5; references 13: 10 Russian, 3 Western (2 by Russian authors).

UDC 541.15;546.790;546.98

**Radiation-Chemical Conversions of Extraction System Components in Presence of Palladium**  
*18410096b Leningrad RADIOKHIMIYA in Russian  
Vol 30 No 5, Sep-Oct 88 (manuscript received 7 Dec 87;  
after final revision 27 Apr 88) pp 618-622*

[Article by V. D. Zaytsev and G. F. Yegorov]

[Abstract] The direction and extent of radiation-chemical reactions occurring in polycomponent extraction systems used for regeneration of highly irradiated nuclear fuel of AES depend on the composition of the solution being processed. Palladium concentration in aqueous phase was studied as it affected radiation-chemical breakdown of the components of two-phase extraction system containing 30% TBP solution in dodecane and an aqueous solution of 1.31 mole/l of uranyl nitrate in 3 mole/l nitric acid. It was shown that in presence of palladium the concentration of nitric acid in irradiated aqueous solution increased considerably; as a result, the yield of organic nitrates was also increased during the irradiation of the two phase system. Palladium did not affect the yields of the nitro compounds

nor of the carboxyl-containing oxidation products. A marked increase in the distribution coefficient of palladium was noted at doses higher than 72 kGy; removal of extracted palladium from organic phase irradiated by a dose higher than 100 kGy was difficult. Hence, the most serious problem for which palladium could be responsible is its ability to form complexes with hydrazine catalyzing its decomposition, formation of precipitates with the products of solvent radiolysis, which could lead to formation of interphase films, and intensification of nitration processes due to higher levels of nitric acid in the irradiated system. Figures 4; references 3: 2 Russian, 1 Western.

UDC 546.791.6:546.655.4

**Coprecipitation of U (VI) and Ce (IV)**  
*18410096c Leningrad RADIOKHIMIYA in Russian  
Vol 39 No 5, Sep-Oct 88 (manuscript received  
18 Sep 87, after final revision 26 Apr 88) pp 628-632*

[Article by Yu. A. Afanasyev, L. T. Azhipa, A. I. Ryabinin and L. P. Kazachek]

[Abstract] A study was undertaken of solid phases forming during coprecipitation of macroquantities of U (VI) and Ce (IV) in the system  $\text{UO}_2^{2+}$  -  $\text{Ce}^{4+}$  -  $\text{NO}_3^-$  -  $\text{H}_2\text{O}$  at different pH values, using different precipitating agents. The character of the solid phases was established by chemical analysis, IR spectroscopy, thermo- and derivato-graphic analysis and x-ray phase analysis. The composition of solid phases varied as a function of pH and the type of precipitating agent was used. In all cases cesium was completely precipitated because of its low solubility. At pH 3.5 uranium precipitated only to the extent of 14%, reaching the high of 66% at pH 5 and 8 in presence of carbonate ions. Uranium was shown to precipitate quantitatively at pH 8 only in the absence of carbonyl ions. Analysis of experimental data indicated that the interaction between uranium and cesium during their coprecipitation had a chemosorptive nature, the solid phases obtained being actually solid solutions of each other with varying composition. Figure 1; references 10: 9 Russian (2 by Western authors), 1 Western.

UDC 669.88.3:541.183.5

**Radionuclide Adsorption With Ferrocyanide Adsorbents. Part 1: Titanium Ferrocyanide as Inorganic Adsorbent**  
*18410096d Leningrad RADIOKHIMIYA in Russian  
Vol 30 No 5, Sep-Oct 88 (manuscript received  
13 Feb 88) pp 644-649*

[Article by V. N. Krylov, S. M. Borisov and A. G. Burov]

[Abstract] The goal of this work was to investigate physical-chemical and adsorption properties of titanium ferrocyanide. Depending on the reaction conditions, either an amorphous or a crystalline form of this reagent

can be obtained. Analysis of powder diffractograms indicated that titanium ferrocyanide is isostructural with  $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ , in which water molecules can be located in open spaces of the crystalline skeleton. However, it was impossible to determine precise water content because it was a function of drying and storage conditions. It was shown that adsorption of cesium ions by titanium ferrocyanide is very complicated: some of the cesium is adsorbed by an ion exchange mechanism leading to liberation of adsorbent protons. One of the characteristics of titanium ferrocyanide is its ability to function in acid media. Cesium adsorption decreased in presence of various salts in the following order:  $\text{NaNO}_3 = \text{NaCl} > \text{Ni}(\text{NO}_3)_2 > \text{Al}(\text{N}_3)_3 > \text{RbNO}_3$ . Figures 3; references 16: 10 Russian (1 by Western author), 6 Western.

UDC 669.882;621.039.325

### Uranium (VI) Ion Adsorption by Cryogranulated Hydroxides of Aluminum, Lanthanum, Bismuth and Iron

18410096e Leningrad RADIOKHIMIYA in Russian  
Vol 30 No 5, Sep-Oct 88 (manuscript received 8 Jun 87;  
after final revision 27 Jan 88) pp 649-655

[Article by V. S. Pakholkov and V. I. Zelenin]

[Abstract] Physical-chemical properties of cryogranulated hydroxides were reported and also their interaction with uranyl ions. Optimal conditions for preparation of these reagents are:  $\text{AlCl}_3$  concentration: 0.1 mole/l; precipitant: 25% aqueous ammonia; duration of the addition of precipitant: 4 s; excess of the precipitating agent: 20%; temperature: -6°C. In respect to acid-base properties, the Al, La, Bi and Fe hydroxides are amphoteric bifunctional ionites. Uranium adsorption of these hydroxides from solutions containing  $\text{UO}_2\text{F}_2$ ,  $\text{UO}_2(\text{NO}_3)_2$ ,  $\text{UO}_2\text{Cl}_2$ ,  $\text{UO}_2\text{SO}_4$  and  $(\text{NH}_4)_4[\text{UO}_2(\text{CO}_3)_3]$  was investigated showing that it increased with an increase of the pH of the medium. Analysis of the IR spectra showed a direct interaction between the OH-groups and uranium in the exchange process, in hydrolysis, condensation of uranium ions and in coordination interaction. An example of a clean separation of cadmium from uranium is given showing great potential of cryogranulated hydroxides of trivalent metals in ion-exchange processes. Figures 6; references 11 (Russian).

UDC 669.822;621.039.325

### Kinetics of Uranium (VI) Ion Adsorption by Cryogranulated Hydroxides of Magnesium, Cadmium, Cobalt and Nickel

18410096f Leningrad RADIOKHIMIYA in Russian  
Vol 30 No 5, Sep-Oct 88 (manuscript received  
9 Feb 88) pp 655-659

[Article by V. I. Zelenin and V. S. Pakholkov]

[Abstract] Analysis was made of experimental and theoretical data from an investigation of the kinetics of uranyl (VI) ion adsorption on cryogranulated Mg, Cd,

Co and Ni hydroxides. Adsorption of uranyl (VI) ions on these hydroxides was accompanied by a formation of hydroxyl complexes as a new phase of uranyl hydroxide and polyuranates. This led to an increased role of the chemical phase contribution to the overall rate of adsorption and in fact became the rate-determining step in some cases. In addition to this, the adsorption rate is affected by the formation of a thin layer of insoluble product from the interaction of uranium ions with active hydroxyl groups of the adsorbent. A mathematical model reflecting these aspects is proposed. The rate of adsorption is expressed as a function of temperature. It was shown that the activation energy which also indicated considerable influence of the chemical phase on the rate of uranium adsorption decreased in the following order:  $\text{Mg}(\text{OH})_2 > \text{Co}(\text{OH})_2 > \text{Ni}(\text{OH})_2 > \text{Cd}(\text{OH})_2$ . Figures 3; references: 11 (Russian, 2 by Western authors).

UDC 621.039.325;669.822

### Kinetics of Uranium (VI) Ion Adsorption on Cryogranulated Hydroxides of Polyvalent

18410096g Leningrad RADIOKHIMIYA in Russian  
Vol 30 No 5, Sep-Oct 88 (manuscript received  
9 Feb 88) pp 660-664

[Article by V. S. Pakholkov and V. I. Zelenin]

[Abstract] Analysis was made of experimental and theoretical data obtained in a study of the kinetics of uranium (VI) ion adsorption on cryogranulated hydroxides of Al, La, Bi, Fe, Ti, Zr and Nb from 0.005 mole/l solutions of  $\text{UO}_2(\text{NO}_3)_2$  and  $\text{UO}_2\text{F}_2$ . Since this process occurs by the mechanism of ion exchange without the formation of any solid phases, a diffusion model was used effectively in describing the kinetics of this adsorption. Activation energy was calculated and shown to be characteristic for an intradiffusion kinetics. Indeed, internal diffusion was shown to be the rate-determining step for all the investigated hydroxides. Figures 3; references: 6 (Russian), 1 by Western author).

UDC 546.681

### Simple Method for High Temperature Isolation of Gallium-67 From Massive Germanium Target

18410096h Leningrad RADIOKHIMIYA in Russian  
Vol 30 No 5, Sep-Oct 88 (manuscript received  
29 Dec 87) pp 672-676

[Article by A. F. Novgorodov, A. Zelinski, A. Kolachkovski, R. Misiak, M. Soveetska, V. A. Ageyev\*, A. G. Belov, M. Kaskevich, A. A. Klyuchnikov\*, A. A. Odintsov\*, and Ye. Mikulski\*\*, \*Institute of Nuclear Studies, UkrSSR Academy of Sciences, Kiev; \*\*Institute of Nuclear Physics, Cracow]

[Abstract] An assumption had been expressed that the most suitable material for the creation of a massive target of multiple utilization (MTMU) for production of Ga-67 is germanium. The problem was to provide a rapid generation method for gallium without substantial losses of MTMU material. There was reason to expect that this could be achieved at pressures ranging from 0.4 to 4.0 atm in an atmosphere of hydrofluoric acid, rather than at high vacuum. The goal of the present work was to rest this assumption. Indeed, a practical method was

developed for quantitative liberation of Ga-67 into the gas phase from proton-irradiated germanium. It required that irradiated germanium be kept in molten state at 1373 plus or minus 10 K in an atmosphere of hydrofluoric acid at about 1.3 atm pressure. Under such conditions germanium evaporation decreased 2-3 fold while Ga-67 separation intensified by an order of magnitude. Figures 3; references 24: 6 Russian (1 by Western author), 18 Western.

UDC 666:621.039.54:0303

**Characteristics of Borosilicate Glass in Simulation of  $\delta$ -Radiation and Thermal Conditions for Storage of Highly Radioactive Vitrified Wastes**  
*18410096i Leningrad RADIOKHIMIYA in Russian  
Vol 30 No 5, Sep-Oct 88 (manuscript received  
1 Sep 87) pp 694-698*

[Article by Ye. S. Prokin, V. S. Kuptsov, T. N. Ananina and Ye. Ye. Yermolayev]

[Abstract] Effect of  $^{238}\text{Pu}$  $\delta$ -irradiation and of thermal treatment of the properties of borosilicate glass with increased content of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  was investigated, this type of glass being used in vitrification of highly radioactive waste (HRW). The composition of this glass was as follows:  $\text{Na}_2\text{O}$  - 22,  $\text{Al}_2\text{O}_3$  - 16.7,  $\text{SiO}_2$  - 14,  $\text{Fe}_2\text{O}_3$  - 1.1,  $\text{MoO}_3$  - 0.1,  $\text{Cr}_2\text{O}_3$  - 0.1 and natural mineral - 45. Finely ground glass was mixed with plutonium dioxide and vitrified at 1150°C to 1200°C for 3 hrs. A control sample without the  $\delta$ -emitter was also prepared. The following properties of this glass were determined: structural state, chemical stability, density, microhardness and evolution of radiogenic helium from the glass. The control glass was amorphous, the samples with the  $\delta$ -emitter exhibited a  $\text{PuO}_2$  phase. Heating this glass to 600°C resulted in partial crystallization of both types of glasses and formation of phases, one of which seemed to be nephelin  $\text{NaAlSiO}_4$ . No changes were observed in any parameters with accumulation of the radiation dose. Figures 4; references 7: 1 Russian, 6 Western.

UDC 676.164.085:2:665.947.2

**Use of Sulfate Turpentine Processing Wastes and Aqueous Wood-Fiber Prehydrolysates in Production of Concrete**

*18410113a Moscow GIDROLIZNAYA I LESOKHIMICHESKAYA PROMYSHLENNOST in Russian No 7, Oct-Nov 88 pp 15-16*

[Article by N. G. Moskovtsev, candidate of chemical sciences, V. F. Slobodyanin, engineer, A. F. Gogotov, candidate of chemical sciences, Siberian Scientific Research Institute of Cement Structures, Yu. P. Karnaughov, candidate of technical sciences, and A. A. Greshilov, engineer, Bratsk Industrial Institute]

[Abstract] The wastes from the chemical processing of wood fiber include "caramel," a copolymer consisting primarily of lignin. Another waste is the still residue from the distillation of sulfate turpentine, a complex mixture of high-boiling-point terpenes, terpene alcohols, and oligomer products of the thermal condensation of monoterpenes. Solutions of the two products together have a number of specific surface-active properties and could be used as air-entraining hydrophobicizing additives for the manufacture of concrete and mortar. Laboratory and field

experiments have confirmed this possibility. Good effects are anticipated for both the economy and the environment. Figure 1, references 7: Russian.

UDC 630\*86:658.62

**Commercial Manufacture of Moisture-Guard Antiseptic Compositions Based on Bakelite and Pitch Varnish**

*18410113e Moscow GIDROLIZNAYA I LESOKHIMICHESKAYA PROMYSHLENNOST in Russian No 7, Oct-Nov 88 pp 24-25*

[Article by A. A. Brashchayko, Svalyavskiy Wood-Chemical Combine, N. V. Fedorova, and V.S. Karasev, Ukrainian Scientific-Production Wood-Processing Association]

[Abstract] The authors' institutions have created and installed a process for the industrial manufacture of moisture-guard antiseptic compositions made of bakelite and pitch varnishes for use in the storage and drying of moist wood materials to prevent cracking and rotting. Author's certificate number 994262 has been awarded for the composition developed. Laboratory testing of the compositions has shown that they fully meet the requirements of state standard GOST 26910-86 and can be used to protect the ends of sawed lumber from cracking and rotting during storage and seasoning. The guaranteed shelf life of the compositions stored in sealed containers and protected from sunlight is 6 months. Projection testing of the specimens showed that, when used according to instructions, they fully protected the wood from cracking and rotting for 3 months. Figure 1.

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